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DEPARTMENT OF CHEMICAL ENGINEERING

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Ozonolysis and Oxyphotolysis
of
Municipal and Industrial Effluents

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20. Abstract
This research deals with the tertiary treatment of effluents using 'OZONE' and the 'OZONE/U.V.' (oxyphotolysis) process. The ozone was either generated insitu at the gas-liquid interface or externally produced and fed into a novel reactor which has a high mass transfer efficiency. The novel reactor uses the 'Hibee' principle of enhanced mass transfer to a thin liquid film as it flows across the surface of a rotating disc. Measurements of mass transfer coefficients for ozone were compared with results calculated from empirical formula derived from previous studies on the hydro-dynamics of such a reactor. Also, tertiary treatment work was carried out and the performance of this rotating disc reactor in contracting ozone with secondary effluents was evaluated. The reactor performed well with these effluents.

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ABSTRACT

This research deals with the tertiary treatment of effluents using 'ozone' and the 'ozone/U.V.' (oxyphotolysis) process. The ozone was either generated insitu at the gas liquid interface or externally produced and fed into a novel reactor which has a high mass transfer efficiency.

The novel technique proved to be the most fruitful area for investigation and hence the research concentrated on this device. It uses the 'HiGee' principle of enhanced mass transfer to a thin liquid film as it flows across the surface of a rotating disc. Measurements of mass transfer coefficients for ozone were compared with results calculated from empirical formulae derived from previous studies on the hydrodynamics of such a reactor. Because ozone is easily dissociated, the effects of pH on ozone absorption were also noted.

In addition to the mass transfer experiments, tertiary treatment work was carried out and the performance of this rotating disc reactor in contacting ozone with secondary effluents was evaluated. The treatment of refractory compounds was typified by the nature of the effluents used in this work, which is a multicomponent effluent consisting of a mixture of domestic and industrial wastes. Samples of potable water supplies with trace amounts of phenol were also used as a good example of a single component effluent. The rotating disc reactor performed well with these effluents.

Experiments were also conducted to determine whether an initial ozone decomposition into radicals is ALWAYS favourable for the oxidation of effluents. A conceptual model, applicable to thin turbulent liquid films with a gas interface, is also proposed to explain the mechanism of ozonolysis of particulates in effluents.

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1   INTRODUCTION

Ozone has been used extensively in Europe for treating and purifying drinking water. Recent studies have shown chlorination of water containing certain organics reactive with chlorine clearly form compounds hazardous to human life. Increasing concern of the end products from chlorination has resulted in a resurgence of interest in ozone. In November 1974, U.S. Environmental Protection Agency (E.P.A.) researchers made public results showing that treating drinking water supplies with chlorine produced many halogenated compounds, some of which might be responsible for causing liver carcinomas. Ozonation has recently been opted in the United States for the less expensive chlorination process. For many years sewage treatment plant effluents in the U.S. have been disinfected with chlorine, supplied either as elemental, gaseous chlorine or as hypochlorite. Later it began to be apparent that discharges of chlorinated effluents from sewage treatment plant to rivers causes severe environmentally detrimental effects upon the aquatic lives in the receiving bodies of water. Some waste products are nonbiodegradable. This has focussed great attention on pretreatment and tertiary treatment processes such as carbon adsorption, ion exchange, solvent extraction, reverse osmosis, chemical oxidation, and others which can be added to conventional waste treatment processes to remove the refractory compounds. No one process has proved to be successful for removing all refractories and, therefore, a combination of chemical and physical treatments will be required. This realisation sparked new interest in the use of ozone for tertiary treatment of secondary effluents. Current studies are being conducted in U.S.A. and Japan to ascertain if ozone utilisation could be increased by using ultra violet radiation in conjunction with ozone. If the treatment time and amount of ozone required could be reduced, an extremely efficient technique might be gained. Spectacular chemical oxidation results have been achieved by workers in the U.S.A. treating certain industrial waste waters with ozone in the presence of ultra violet irradiation. Previous investigators normally study the use of ozone for effluent treatment on a single pollution parameter. Very little work has been carried out on the overall effects of ozonation on multiple component effluents such as municipal waste containing highly refractory compounds which are more universally encountered. Even so, it is important to note that the reaction mechanism of ozone varies with the organic species with which it reacts.

With the above considerations in mind, this research firstly attempted to investigate the feasibility of the simultaneous production of ozone and treatment of liquids in

electrical discharges at atmospheric pressure. Ozone was
generated at the surface of a falling film. However, because
these results were not as spectacular as hoped, owing to
inefficient mass transfer, a more comprehensive study of the
effect of ozone and U.V. was carried out on a variety of
effluents using a novel technique for mass transfer, with the
hope that this would identify the mass transfer parameters
and mechanisms preventing good 'insitu' treatment. A
'Rotating Disc Reactor' developed in this department was used
as the contactor because in the past, it has been shown that
such a contactor is very efficient in mass transfer and
because good mass transfer data was available for this
reactor when used with other gases.

Further work on 'insitu' generation and treatment will be
required using this efficient mass transfer technique before
the feasibility of 'insitu' techniques can be proven.
Because the results obtained with the rotating disc reactor
were encouraging, it was decided to concentrate on this
technique at the expense of 'insitu' experiments, with the
recommendation that the two techniques will be combined when
the performance of the rotating disc reactor is fully
understood.

1.1 SCOPE OF RESEARCH

The work was divided into two essential parts :

1. Generation of ozone in reactors with large electrode
    separation and at the surface of a fluid.

2. Studies on the treatment of a refractory bearing effluent
    using externally generated ozone in conjunction with a
    highly efficient mass transfer contactor.

It is proposed to cover both aspects of the work in two
distinct parts, namely Part I (covered in Chapter 2 and
Appendix A) and Part II (covered in Chapters 3 - 10).

2   PART I : IN SITU OZONE GENERATION AND TREATMENT OF INDUSTRIAL
                EFFLUENTS

   This research attempts to investigate the feasibility of
the simultaneous production of ozone and treatment of liquids
in electrical discharges at atmospheric pressure. Factors
affecting ozone production by electrical discharges, such as
the sharpness of points, the diameter of wires and the length
of the discharge electrodes were studied in the
point-to-plane model and the co-axial model
(wire-in-cylinder).

   Several preliminary experimental studies were conducted to
attempt to generate ozone either within gas bubbles formed on
the discharge electrodes under water, or to generate ozone
over the surface of a falling liquid film. A nanosecond
pulse generator capable of supplying high voltage (25 kV),
large current pulses with rise times of about 10.0
nanoseconds was used.

   Interest in atmospheric pressure electrical discharges has
grown in recent years due to the economic advantages of
operating commercial plasma processing devices at atmospheric
pressure. The preliminary experiments carried out in the
attempt to investigate the feasibility of simultaneous
generation of ozone and treatment of liquids in electrical
discharges are reviewed within this section.

2.1   SCOPE OF STUDIES

   1.   Characteristics of Electrical Discharges in
        Point-to-Plane Model.

   2.   Characteristics of Electrical Discharges in Coaxial Model
        (Wire-in-Cylinder).

   3.   Factors affecting high voltage nanosecond pulse
        generation.

   4.   Generation of ozone in the presence of water.

   5.   The treatment of a refractory compound (typified by dyes)
        when ozone is generated at a liquid surface.

2.2   THE MECHANISM OF OZONE GENERATION

In the formation of ozone from air or oxygen, precursors of ozone are excited O-atoms, produced by the electronic dissociation of oxygen :

$$O_2 + e \longrightarrow O + O^* \longrightarrow O + O + h\nu \quad \ldots\ldots(2.1)$$
$$O + O_2 \longrightarrow O_3 \quad \ldots\ldots(2.2)$$
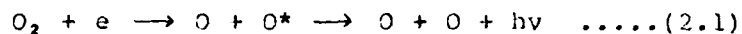
The dissociation of ozone occurs simultaneously :

$$O_3 + e \longrightarrow O_2 + O + e \quad \ldots\ldots(2.3)$$
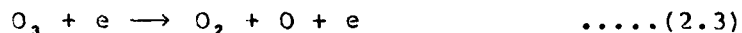
When a sufficiently high electric field is applied to a gas, an electron avalanche develops at a rate depending on the applied electric field, the source impedence of the power supply and the physical properties of the gas. If the field is sustained, the avalanche normally develops into an arc. To prevent breakdown, commercial ozonisers make use of a dielectric material. Because of the nature of the silent discharge, such ozonisers are able to pulse themselves. This pulsing mechanism retards the consequence of Reaction 2.3.

Earlier work carried out in the U.S.A. (1) shows that ozone/U.V. oxidation is more efficient than ozonolysis alone. This is due to the formation of highly reactive radicals (O atoms, OH, HO_2) and excited state species when ozone is irradiated by U.V.:

$$O_3 + h\nu \longrightarrow O_2 + O^* \quad \ldots\ldots(2.4)$$

This reaction is the reverse of the formation process (Eqn. 2.2) in conventional ozonisers.

O atoms are precursors of ozone. Also, OH and HO_2 radicals are decomposition products when ozone decomposed in the presence of liquid. Therefore, any process which enable the generation of all these species at the gas/liquid interface should produce an enhanced reaction rate.

From the above considerations it would seem to be desirable to generate ozone in situ at a liquid surface. However because of the small electrode separations involved, conventional ozonisers are not suitable for insitu genaration. Attempts to produce ozone in generators with large electrode separations fall into two categories :

1. Dieletricless D.C. systems.

2. Dielectricless Pulsed systems.

These are detailed below.

2.3   OZONE GENERATION IN DIELECTRICLESS D.C.   REACTORS

Measurements were carried out to investigate the important characteristics of D.C. systems. Work on Pt-to-Plane and Wire-in-cylinder models were carried out. The results were not as encouraging as in Dielectricless Pulsed Reactors. It is not proposed to detail this here but the main conclusions are set out in Appendix A.

2.4   THE ELECTRICAL CIRCUIT OF THE HIGH VOLTAGE NANOSECOND PULSE
GENERATOR

To minimise dissociation of ozone by impact of electrons, the duration during which electrons appear in the discharge gap should ideally be smaller than the formation time of ozone. If an overvoltage much greater than the static breakdown voltage is applied to a non-uniform field, avalanches will develop from a large number of emission sites. The voltage is then reduced after an appropriate time interval to prevent any avalanche developing into an arc. The desirable pulse shape is shown in Fig.(1). The risetime of the pulse (0 - T1) should be about 10 nanoseconds to cause the formation of electron avalanches from a large number of emission sites. From T1 - T2, the avalanches are developing and the resulting increase in current causes the voltage to fall. The duration of the pulse, 0 - T2, should be small so that an arc fails to develop. A short-duration high-power pulse ensures that the radicals produced from one pulse will not react with radicals produced by the preceeding pulse.

Work carried out in this Department on the mechanism of ozone formation in conventional ozonisers has led to collaboration with the Department of Electrical Engineering, University of Newcastle upon Tyne, in the development of pulsing units capable of supplying 26 kV pulses, with risetimes of less than 10 nanoseconds (2).

The source of power for the pulse generator is a 50 kV, 1 mA, D.C. supply unit (Brandenburg High Voltage Generator, Type MR.50/RA.). The charging current was limited to about 1 mA by means of a 10 MΩ charging resistor (R_c). The generator consists of two identical stainless steel spark gaps (G_0 and G)

connected in series, Fig.2. The capacitor C_c (1300 pf) was charged by the D.C. supply and when fully charged, breakdown in the gap G_o occurs. G_o was set at 3.5 mm. The static breakdown voltage for this setting in air is about 20 kV. G_o has a relatively slow breakdown time due to the relatively large charging time constant (R_c x C_c = 10 x 10^6 x 1300 x 10^{-12} = 13 ms, i.e., a slow rising ramp voltage across the capacitor C_c). The resulting pulse obtained is then sharpened by a second spark gap, G_s, set at 0.7 mm. The second gap is the pulse sharpening gap used to reduce the risetime of the pulse. Its breakdown process should start immediately after the breakdown of G_o has stopped. The breakdown of G_o was decreased by connecting a capacitor C_o across it. C_o was constructed by connecting three 13 cm long co-axial cables in parallel. When G_o breaks down, C_o discharges into the gap, thus increasing the breakdown channel conductivity. This results in the reduction of the breakdown time, i.e. improving the risetime of the pulse. Hence a fast rising pulse could be obtained across the load.

The leakage resistor, R_o, maintains the connection between the two gaps at earth potential in between breakdowns. The damping resistor, R_d, has no effect on the pulse generated. The 5-meter co-axial transmission cable acts as a capacitor, giving a capacitance of about 50 pf/m.

2.5 OZONE GENERATION IN DIELECTRICLESS PULSED REACTORS

The silent discharge method is the most efficient method of ozone generation. However, due to the narrow discharge gap, it is difficult to control the current pulse train in such ozonisers. To attain a controlled corona discharge (silent discharge), a dielectric material is used so as to cause the glow to spread uniformly and prevents an early breakdown into brush and arc discharge. As a consequence, the resistance of the discharge gap between the electrodes is increased, thereby resulting in a higher voltage being required to maintain the discharge.

This problem can be solved by using fast-rising pulsed current in conjunction with a dielectricless ozoniser. The dielectricless ozoniser would need to have sharp edge electrodes to maintain a corona discharge. Work on the point-to-point discharge (Appendix A) shows that a corona discharge can be maintained with D.C. but this will eventually arc down when high voltage D.C. potentials are applied. Vahid (3) designed a metal-to-metal ozoniser consisting of a number of discs with sharp edge along the axis of an earth cylinder, Plate 1. He showed that D.C. and

Fig 1 :   Desirable Pulse Shape

R_c = charging resistor, 10 MΩ
C_c = charge condenser, 1300 pf
G_o = spark gap
C_o = condenser, 30 pf
R_o = leakage resistor. 13.2 MΩ
G_s = spark gap
R_d = damping resistor
L_d = co-axial cable, 50 pf/m
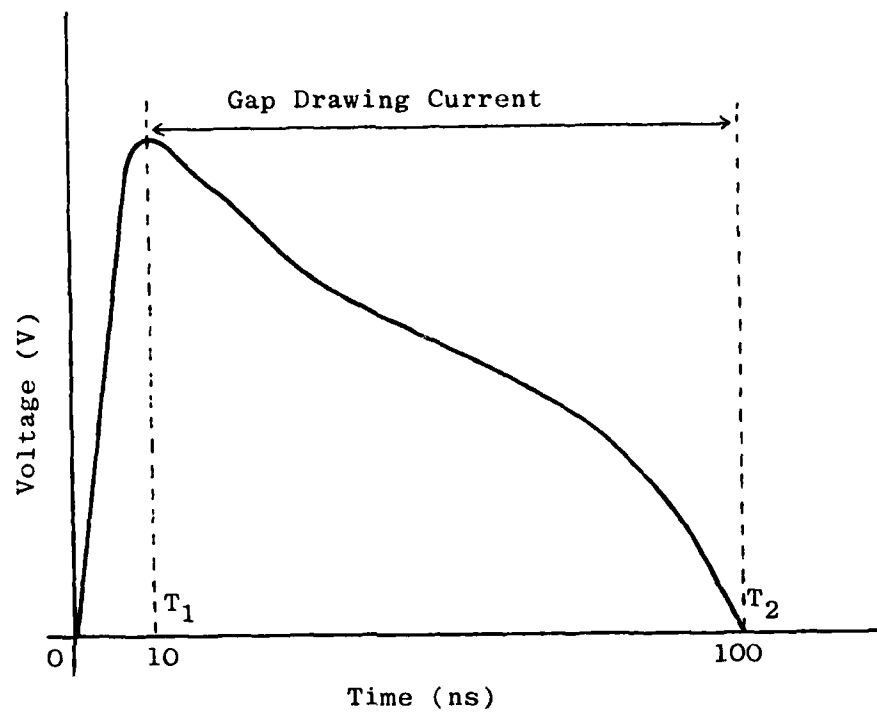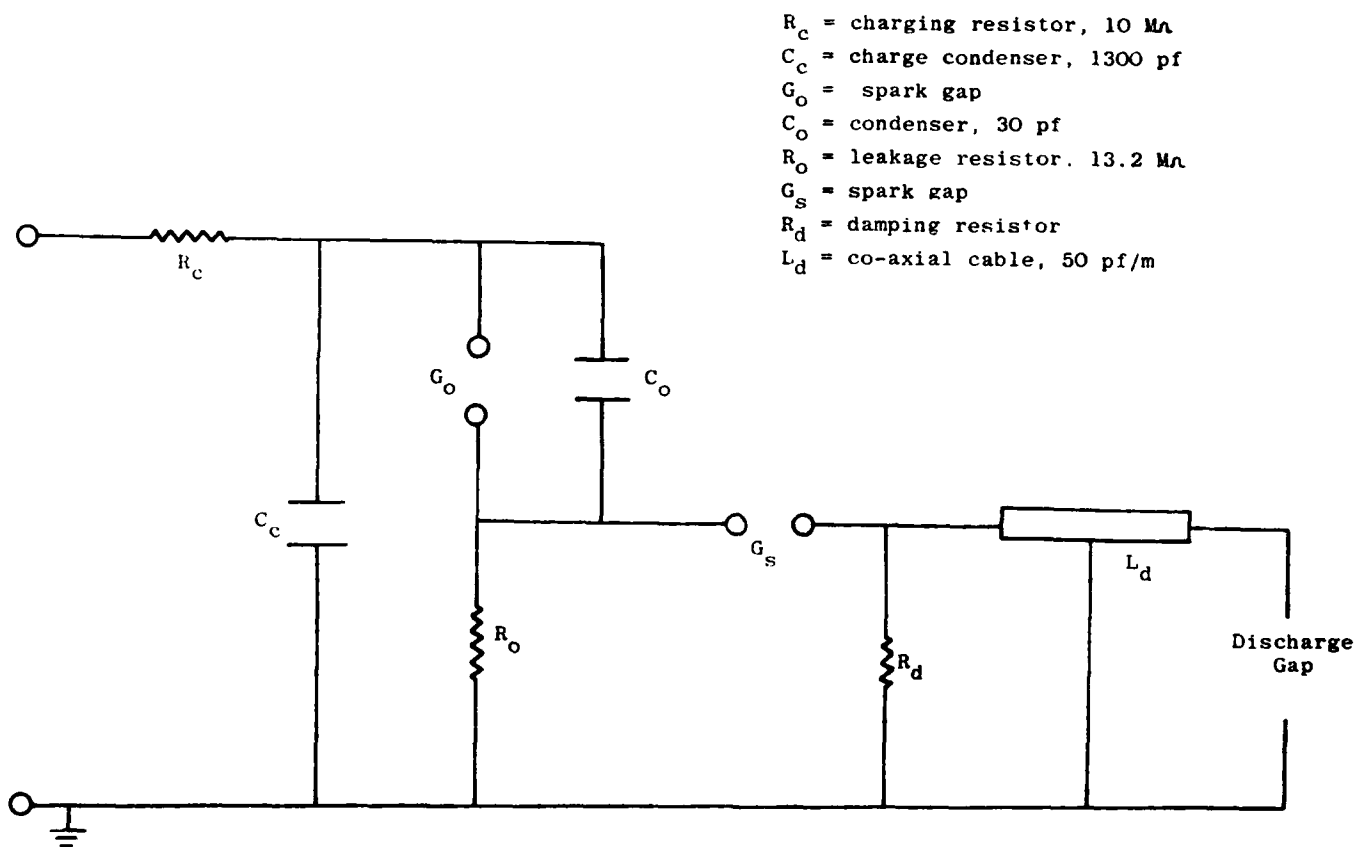
Fig. 2 : Circuit Diagram of nanosecond Pulse Generator
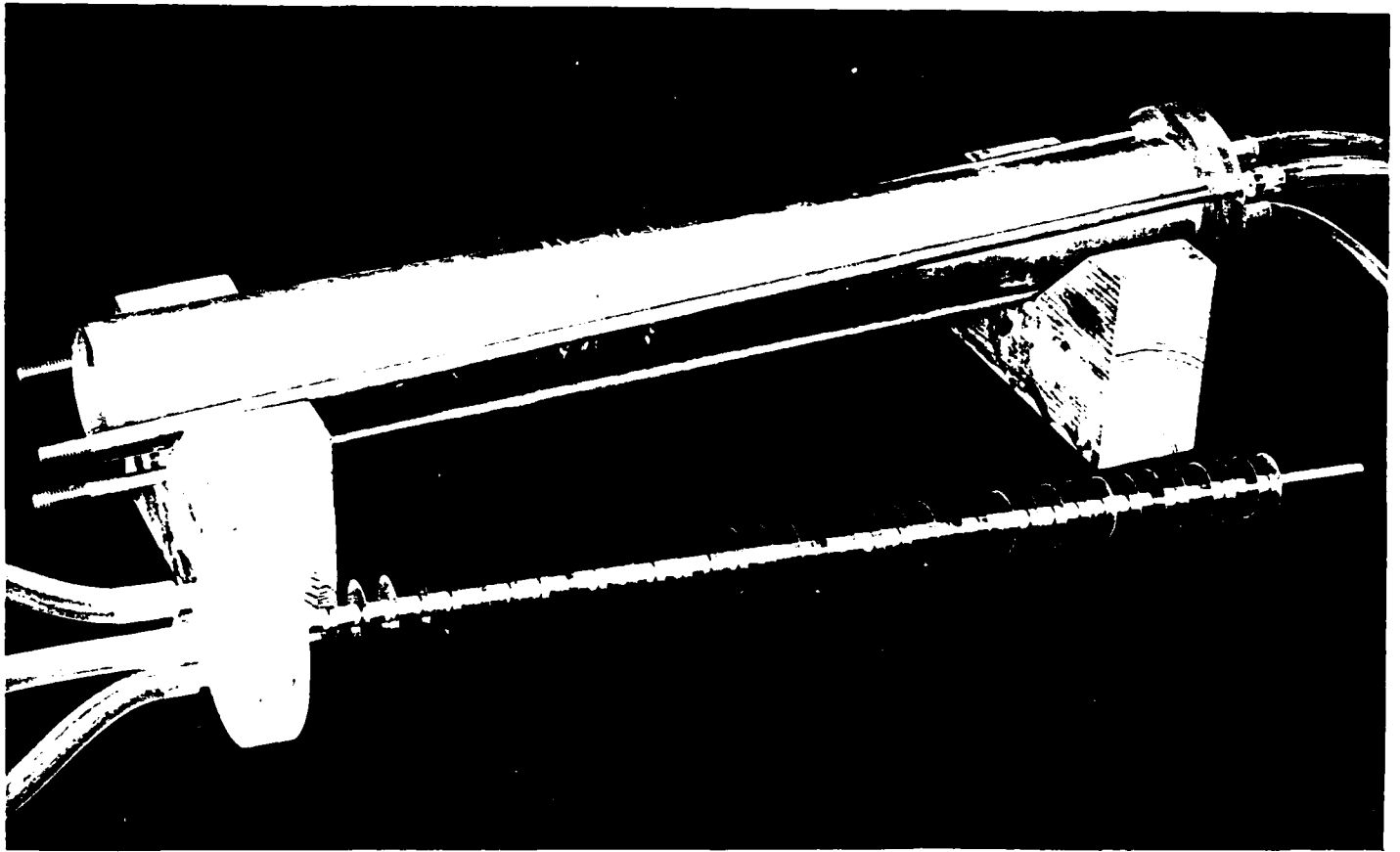
A.C. power have only a small range of operation before arcing occurs, but with a nanosecond pulse generator, it is capable of generating ozone with an energy yield that is compatible with conventional ozonisers. The short pulses allow a much higher electric field to be applied under identical physical conditions. The geometry of this dielectricless ozoniser has the advantage of being able to tolerate a higher level of moisture in the feed gas without a dramatic loss in ozone production. This is attributed to the larger discharge gap used, 12.0 mm, as compared to 2.0 - 4.0 mm in a conventional silent discharge ozoniser.

2.6   GENERATION OF OZONE IN THE PRESENCE OF WATER

Preliminary work with the pulsing power supply showed that it is possible to generate ozone within discrete bubbles formed at hollow needle electrodes under water. Having established the fact that ozone can be generated under water, it was anticipated that a falling film reactor would be more practical in terms of scale-up, and hence the dielectricless ozoniser refered to in Section 2.5 was modified to enable a free falling liquid film to flow down the inside of the earthed cylinder. Pulsing enables ozone generation in the presence of liquid without the apparatus short circuiting.

The objective of this experiment is to generate ozone using electrical pulses at the surface of the effluents. This will have all the benefits of immediate chemical reactions by ozone and its intermediates (excited state species) and usefully utilises the U.V. generated as a "by-product" of the ozone generation process. Hence the ensuing treatment will have all the benefits of the oxyphotolysis (ozone/U.V.) technique, and possibly electrically enhanced mass transfer as well. Free radicals produced in an electric discharge tend to react with each other more rapidly than with anything else. Therefore insitu generation of ozone will ensure maximum usage of the free radicals at the gas/liquid interface to promote chemical reactions.

The effects of pulse parameters (peak voltage, peak current, pulse generator spark gaps) on ozone production were studied to obtain the optimum settings. The risetime of the pulse obtained was about 10.0 nanoseconds, with a pulse duration of about 500.0 microseconds and a peak voltage of about 25.0 kV. The interval between pulses is about 2.5×10^{-2} seconds for a 12.0 Watt power input measured on the D.C. generator.

To compare the efficiency of oxidation using ozone generated insitu with ozone generated externally, a free falling liquid film is allowed to flow down the inside of the ozoniser. The first set of runs were performed with ozone generated insitu. Dye solutions were used to simulate refractory bearing liquids.

The ozone for the second set of runs was supplied to the reactor (through which the dye recirculated) from an external ozoniser. The same ozone concentration was used in both experiments. Liquid samples were taken at certain time intervals and their absorbance/transmittance measured with a Unicam SP800 spectrophotometer.

Fig.(3) shows that treatment by ozone generated "insitu" is better than when it is supplied from an external source. Since the ozone input into both systems are essentially identical, the "insitu" method of treatment must be intrinsically conducive for the treatment of effluents. This may be attributed to :

1. Improved mass transfer of ozone due to simultaneous production and absorption at the gas/liquid interface.

2. Ultra-violet photolysis promoted by the U.V. generated by the discharge generates more excited state species which are not normally produced by ozonolysis alone.

3. Removal of free radicals by the liquid film reactions before their recombinations.

4. The precursors of ozone (O atoms) may be carrying out the oxidation simultaneously with ozone.

5. Ultra-violet radiation excites the dye molecules, i.e. U.V. activates the molecules, rendering them more susceptible to oxidation by ozone.

With this apparatus it is not feasible to identify which of the above has the greatest influence. Therefore it was decided to carry out a more comprehensive study on the factors influencing ozone oxidation in thin films without the addition complication of ozone intermediates. This work is detailed in Part II of this report.

2.7 CONCLUSIONS

Although the results obtained in this work on the feasibility of the simultaneous production of ozone and treatment of liquids in electrical discharges were very encouraging, there was no conceivable way that the present configuration could be scaled to a practical size required for treatment of effluents. For this reason and because it is desirable to have a 'controlled' liquid film, the idea of the 'rotating disc' reactor (4) was proposed. Liquid films produced by centrifugal forces on rotating surfaces can be controlled more effectively than those formed under the action of gravity on stationary planes.

2.8 RECOMMENDATIONS FOR FUTURE WORK

The risetime of the pulse generator used in this work cannot be improved beyond a certain value (about 10.0 nanoseconds) by improving the switching mechanism (i.e. the spark gaps). The risetime was limited to this value by the residual inductance (L) of the pulse generator (i.e. the L/R time constant). The inductance and capacitance increases with an increase in dimensions of the apparatus. Hence the requirements of fast risetime and short duration pulses are contrary to achieving high voltage pulses. This is due to the fact that as the voltage and current are increased, the dimensions of the pulse generator will have to be increased and this will result in an increase in stray capacitance and residual inductance. This limitation can be overcome by reducing the residual inductance of the pulse generator with a completely different geometry - a coaxial geometry.

The factors affecting pulse parameters in this new design have been analysed in the Department of Electrical Engineering, University of Newcastle upon Tyne, (5,6). This new design is capable of generating pulses with risetime of about 7.0 nanoseconds. A theoretical possibility to increase the breakdown voltage of the gas insulated spark-gap is the augmentation of the gas pressure. More work should be carried out to investigate this phenomenum.

Ozone Conc. = 1.3 mg/1.

OZONE GENERATED EXTERNALLY

INSITU TREATMENT

ABSORBANCE x 0.1

TIME - MINS
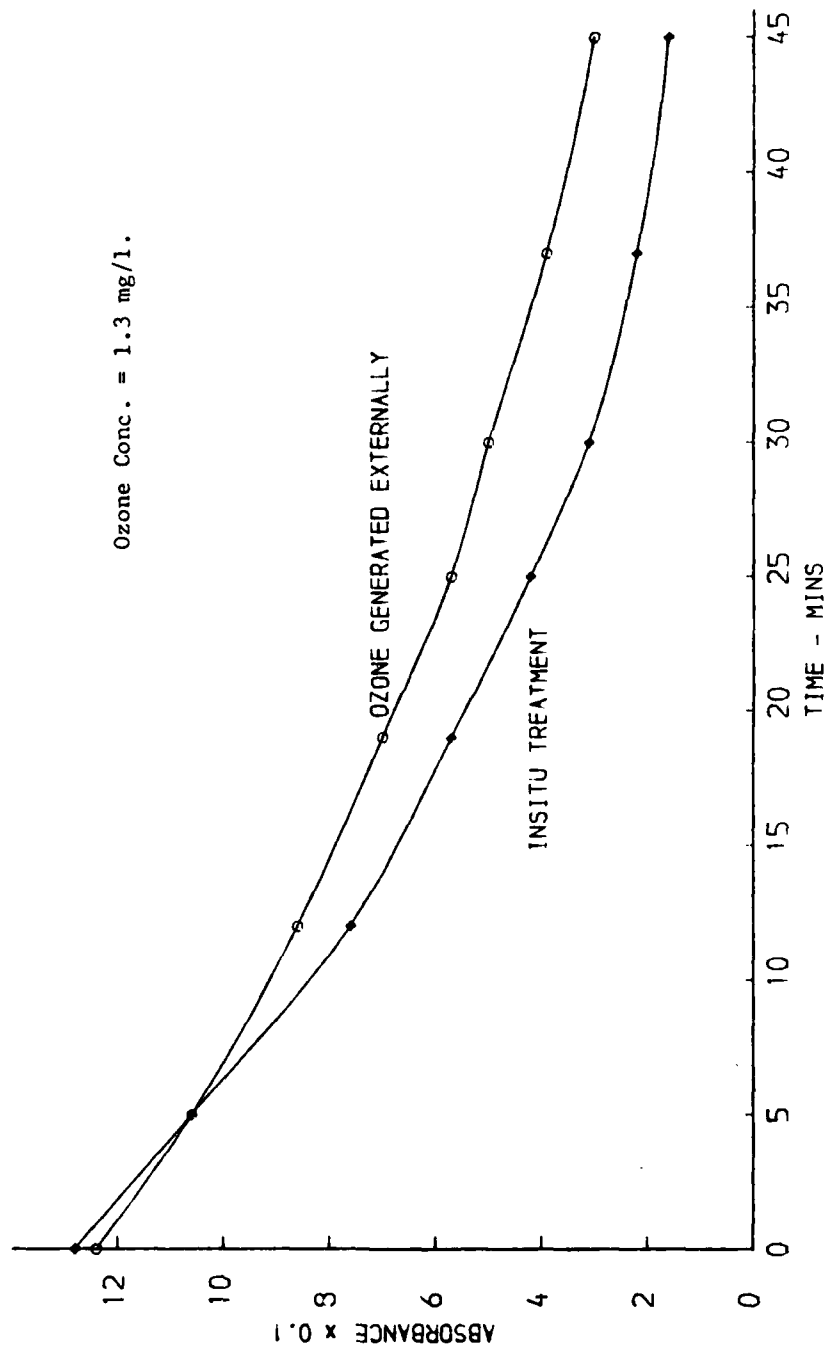
FIG. 3. ABSORBANCE VS. TIME

3   PART II : OZONOLYSIS AND OXYPHOTOLYSIS OF EFFLUENTS USING A
            SPINNING DISC REACTOR

3.1   SCOPE OF STUDIES

1.   Mass transfer studies using a rotating disc contactor

     a.   To determine the rate of solution of ozone in water
          at a certain temperature.

     b.   To study the relationship between the liquid phase
          ozone concentration and the gas phase ozone
          concentration ,i.e. its distribution coefficient.
          This data will give us an indication of the liquid
          phase ozone concentration to be expected for given
          concentrations of applied ozone at a particular
          temperature.

     c.   To test the validity of a design equation developed
          for absorption of oxygen by a rotating disc reactor.

     d.   To investigate the effects of pH on the decomposition
          of ozone in water and to correlate these results with
          the results obtained from experiments on the effects
          of pH on the treatment of effluents.

2.   Ozonolysis of Multicomponent Refractory Bearing Effluents

     a.   To investigate whether ozone could be used as an
          effective tertiary treatment process for this class
          of effluents. A few measurements were also made with
          primary effluents as a comparison with the tertiary
          treatment results.

     b.   To determine whether ozone could be used as an
          effective oxidant for the removal of highly coloured
          effluents which seem to be resistant to the
          conventional means of treatment.

     c.   To determine whether conditions which accelerate an
          initial ozone decomposition into radicals prior to
          oxidation are ALWAYS favourable for the oxidation of
          refractory impurities in effluents.

     d.   To study the mechanism of ozonolysis of particulates.

3. <u>Ozone/U.V.</u> oxidation <u>of Refractory Bearing</u> effluents

    a.   To compare the difference in degree of treatment of effluents with 'ozone' and 'ozone/U.V.' oxidation.

    b.   To compare the effects of ozone and U.V. on multicomponent effluents compared to that of a single component.

The effluents used in this work are:

1.   A multicomponent effluent taken from both the primary and secondary stage of an activated sludge treatment plant that treats mixed domestic and industrial wastes.

2.   A highly coloured multicomponent effluent.

3.   A single component effluent comprising of water containing traces of phenol to typify a contaminated potable water supply.

4 LITERATURE REVIEW ON OZONE TECHNOLOGY

4.1 DECOMPOSITION OF OZONE IN THE GAS AND LIQUID PHASES

Ozone readily dissociates in both the gas and liquid phases. Thus it is necessary to consider the mechanism of dissociation in both phases.

The mechanism of thermal gas phase decomposition of ozone is :

$$O_3 + M \underset{K_2}{\overset{K_1}{\rightleftharpoons}} O_2 + O + M \qquad \ldots\ldots\ldots\ldots(4.1)$$
$$O + O_3 \overset{K_3}{\longrightarrow} 2\,O_2 \qquad \ldots\ldots\ldots\ldots(4.2)$$
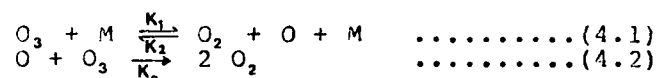
where M is a third body present in the gas phase :- oxygen, ozone, nitrogen, carbon dioxide, helium or whatever is present (7). Apparently, the decomposition of ozone at room temperature also depends on surface reactions. In clean vessels made of inert materials , a half-life of 20-100 hours may be obtained.

The liquid phase decomposition is much more rapid than in the gaseous state. Weiss (8) proposed as a first step the reaction :

$$O_3 + OH^- \longrightarrow O_2^- + HO_2 \qquad \ldots\ldots\ldots\ldots(4.3)$$
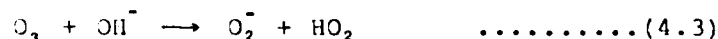
being followed by the chain reactions :

$$O_3 + HO_2 \longrightarrow 2\,O_2 + OH \qquad \ldots\ldots\ldots\ldots(4.4)$$
$$O_3 + OH \longrightarrow O_2 + HO_2 \qquad \ldots\ldots\ldots\ldots(4.5)$$
$$HO_2 + HO_2 \longrightarrow O_3 + H_2O \qquad \ldots\ldots\ldots\ldots(4.6)$$
$$HO_2 + OH \longrightarrow O_2^- + H_2O \qquad \ldots\ldots\ldots\ldots(4.7)$$
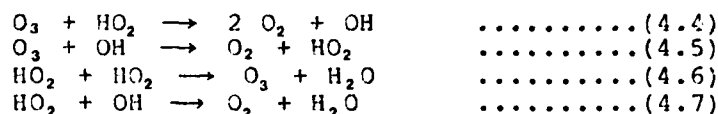
Weiss (8) calculated that the kinetics of ozone decomposition should be a 3/2 rate constant with respect to ozone concentration.

However, on the basis of their kinetic studies, Alder and Hill (9) suggested a first order reaction with respect to ozone concentration and proposed the following mechanism :

$$O_3 + H_2O \longrightarrow HO_3^{\bullet} + OH^- \qquad \ldots\ldots\ldots\ldots(4.8)$$
$$HO_3^- + OH^{\bullet} \longrightarrow 2\,HO_2 \qquad \ldots\ldots\ldots\ldots(4.9)$$
$$O_3 + HO_2 \longrightarrow HO + 2\,O_2 \qquad \ldots\ldots\ldots\ldots(4.10)$$
$$HO_2 + HO \longrightarrow H_2O + O_2 \qquad \ldots\ldots\ldots\ldots(4.11)$$
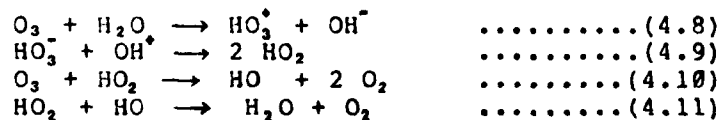
The reaction between water and ozone in the vapour phase has been investigated by McGrath and Norrish (10), Norrish and Wayne (11), who observed strong OH absorption bands in the flash photolysis of ozone-water mixtures and proposed that OH radicals are formed by reaction with the O radical :

$$O_3 + h\nu \longrightarrow O_2 + O \qquad \ldots\ldots\ldots(4.12)$$
$$O + H_2O \longrightarrow 2\ OH \qquad \ldots\ldots\ldots(4.13)$$

Based on reactions (4.12) and (4.13), it appears reasonable to assume that a likely mechanism for ozone decomposition in water is :

$$O_3 + H_2O \longrightarrow O_2 + 2\ OH \qquad \ldots\ldots\ldots(4.14)$$
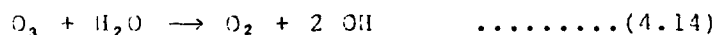
The hydroxyl radical (OH) would then react as follows:

$$OH + O_3 \longrightarrow HO_2 + O_2 \qquad \ldots\ldots\ldots(4.5)$$

to produce the hydroperoxyl radical (HO_2) which could react :

$$HO_2 + O_3 \longrightarrow OH + 2\ O_2 \qquad \ldots\ldots\ldots(4.4)$$
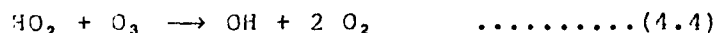
similar to the reaction scheme previously proposed by Weiss (3). The hydroxyl radicals may dimerize to form hydrogen peroxide (Thomas, 12) :

$$OH + OH \longrightarrow H_2O_2 \qquad \ldots\ldots\ldots(4.15)$$

and to further react with hydrogen peroxide :

$$OH + H_2O_2 \longrightarrow HO_2 + H_2O \qquad \ldots\ldots\ldots(4.16)$$
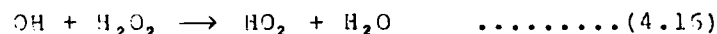
The hydroxyl and hydroperoxyl radicals are also reported to react with each other in the following manner (Czapski et al., 13) :

$$OH + HO_2 \longrightarrow H_2O + O_2 \qquad \ldots\ldots\ldots(4.17)$$
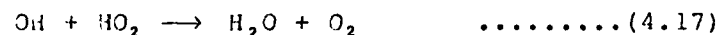
In alkaline solutions the following reaction becomes increasingly important (Hochanandal, 14) :

$$OH + OH^- \longrightarrow O^- + H_2O \qquad \ldots\ldots\ldots(4.18)$$
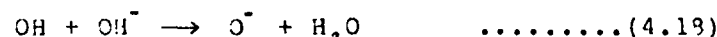
The oxide radical ion, in contrast to the hydroxyl radical, can react with oxygen to form the ozonide ion (Adams,G.E. et al., 15) :

$$O^- + O_2 \longrightarrow O_3^- \qquad \ldots\ldots\ldots(4.19)$$

Like the hydroxyl radical, the hydroperoxyl radicals have also been reported to dimerize in aqueous solution

(Czapski,G., et al., 13) :

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2 \qquad \ldots\ldots\ldots(4.20)$$
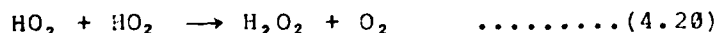
disagreeing with reaction (4.6) suggested by Weiss (8).

From the above review, the following stages for ozone decomposition in aqueous solution is suggested as applicable for this work :

$$O_3 + H_2O \longrightarrow O_2 + 2\ OH \qquad \ldots\ldots\ldots(4.14)$$
$$O_3 + OH \longrightarrow O_2 + HO_2 \qquad \ldots\ldots\ldots(4.5)$$
$$O_3 + HO_2 \longrightarrow 2\ O_2 + OH \qquad \ldots\ldots\ldots(4.4)$$
$$OH + OH \longrightarrow H_2O_2 \qquad \ldots\ldots\ldots(4.15)$$
$$OH + HO_2 \longrightarrow H_2O + O_2 \qquad \ldots\ldots\ldots(4.17)$$
$$OH + OH^- \longrightarrow O^- + H_2O \qquad \ldots\ldots\ldots(4.18)$$
$$O^- + O_2 \longrightarrow O_3^- \qquad \ldots\ldots\ldots(4.19)$$
$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2 \qquad \ldots\ldots\ldots(4.20)$$
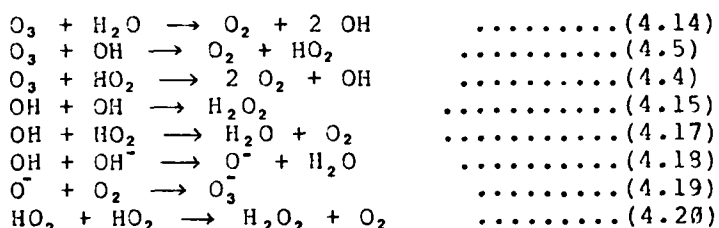
The decomposition of ozone in water is complicated , depending on the alkalinity of the solution and possibly also on the oxygen content. All of the intermediate species formed are very reactive and possess very short half-lives, $(1 \times 10^{-4} sec)$.

Hence the possible species to be found in aqueous ozone solution are O_3, OH, HO_2, O^-, O_3^-, and possibly the free oxygen atom if the ozone decomposes as in reaction (4.1) before reacting with the water.

4.1.1 Oxidation Potential of Ozone and its Decomposition Products

Ozone has an oxidation potential of 2.07 V. Baxendale (16) gives a value for the oxidation potential of the hydroxyl radical as 2.8 V and 1.7 V for the hydroperoxyl radical, which suggests that the OH radical in water might be the species possible for the strong activity of ozonated solution and not the free ozone itself. Comparisons of the reactions of the hydroxyl radicals and ozone indicate a strong similarity. For example, ozone reduces the organic content of wastewater effluents (Hewes & Davidson, 17), and a similar effect was observed using the OH radical (Bishop et al., 18).

The chemical activity of the basic form of the hydroxyl radical, the oxide radical ion O^-, differs markedly from that

of the OH in many reactions. While the hydroxyl radical adds readily to aromatic molecules, the reactivity of O^- toward aromatic compounds is lower by at least three orders of magnitude in the specific rate constant (Czapski, 19). The OH radical is much more effective than is the oxide radical ion in oxidising a number of inorganic ions (Dorfman & Adams, 20). The hydroperoxyl radical (HO_2) has been shown to be almost inert in aqueous solution towards organic substances such as ascobic acid (Barr & King, 21). Limited studies on the ozonide radical (Czapski, 19) have shown that it is almost totally unreactive to aromatic molecules, as well as to methanol and ethanol.

Thus, the hydroxyl radicals are the most reactive oxidant present in the water.

4.2 THE ROLE OF HYDROXYL RADICALS IN OZONATION PROCESSES

During ozonation, part of the ozone dissolved in water reacts directly with the solutes. Such 'direct reactions' are highly selective and often rather slow (minutes). However ozone may also decompose in water before reacting with solutes. This decomposition leads to more reactive species which determine the subsequent oxidation reactions. Based on experimental results published by Weiss (3), Stumm (22), Kilpatrick et al. (23), and others, this decomposition of ozone is the result of a chain reaction in which hydroxide ions act as chain initiators. Free radicals (eg. OH radicals) produced by reactions may be involved as chain carriers . It is now generally accepted that the decomposition of ozone thus leads to free radicals. Among these, the OH (hydroxyl) radicals belong to the most reactive oxidants known to occur in water. They easily oxidise even inert types of organic solutes, but they are non selective and become consumed via fast reactions.

Hewes and Davidson (24) postulated a probable mechanism for the reaction of OH radicals with organics :

$$RH + OH \longrightarrow R^{\bullet} + H_2O$$
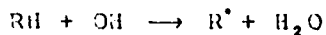
This could be followed by a process of autoxidation as described by Jri (25) :

$$R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet}$$
$$RO_2^{\bullet} + RH \longrightarrow ROOH + R^{\bullet}$$
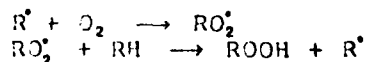
The hydroperoxides might also decompose as follows :

$$2 \ ROOH \longrightarrow H_2O + RO^{\cdot} + RO_2^{\cdot}$$
$$ROOH \longrightarrow RO^{\cdot} + OH$$
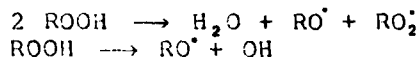
The chain terminating reactions would be :

$$2 \ RO_2^{\cdot} \longrightarrow products \quad (CO_2 + H_2O + other \ oxides)$$
$$RO_2^{\cdot} + R^{\cdot} \longrightarrow products \quad (CO_2 + H_2O + other \ oxides)$$
$$2 \ R^{\cdot} \longrightarrow products \quad (CO_2 + H_2O + other \ oxides)$$
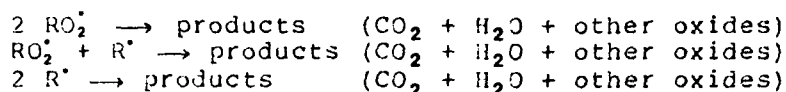
Hewes found that the reaction rate of ozone with dissolved organic compounds seems to depend on the quantity of ozone decomposing rather than on the concentration of the dissolved ozone, except insofar as the decomposition depends on concentration. It seems likely that the main reacting species are the free radicals formed by ozone decomposition.

According to Hoigne and Bader (25), ozone may either react directly with solutes or, above a critical pH value, decompose prior to reaction with solutes. Beyond this critical pH value decomposition products of ozone such as hydroxyl radicals (OH) become the important oxidants. The critical pH value above which the second type of reaction predominates depends on both the rate with which ozone reacts directly with the substrates and on the solutes present in the water (including reaction products) that will enhance or retard ozone decomposition.

Some types of specified solutes are expected to become easily oxidised by the 'direct-type' reaction of molecular ozone present during ozonation. Some types of solutes, react with OH radicals and form secondary radicals (R$^{\cdot}$) which also act as radical chain-carriers. Other solutes quench the 'radical-type' chain reaction. The nature of the reaction thus depend on the sort of effluents treated. Hence part of the aim of this project is to determine whether conditions which accelerate an initial ozone decomposition into radicals are favourable for the oxidation of a typical refractory bearing effluent.

5 OZONE/ULTRA-VIOLET OXIDATION (OXYPHOTOLYSIS)

The prior art of water purification includes both ozone portable water purifers and ultraviolet water purifiers. It is also known to subject contaminated water to both ozone treatment and ultraviolet radiation treatment, but this is normally carried out at separate locations or sequentially with respect to time. However, only recently have investigations into the combined use of U.V. and ozone been conducted (Zeff,J.D., et al., 27). It has been shown that there is a synergistic effect between the ozonation of the water and the ultra-violet irradiation of the water, when these are done simultaneously.

5.1 CHEMISTRY INVOLVED IN OZONE PHOTOLYSIS

Photochemistry is concerned with the chemical and related physical effects of electronic excitation initiated primarily by ionising radiation from ultraviolet (U.V.) and visible light. The absorbance of radiation by a molecule elevates the absorbing species to a higher energy level. The species is usually unstable at the new energy level and by a deactivation process it reverts to a less energetic, and more stable state. The deactivation pathway followed by a particular molecule is peculiar to its chemical species and to the frequency of the radiation absorbed. The excited electronic state may result in certain electrons no longer maintaining a chemical bond between atoms. When the bond breaks as a result of the absorption of a quantum of radiation, free radicals usually are formed. It is the free radicals that initiate further chemical reactions. The lifetime of the excited state before the molecule returns to the ground state is very short, of the order of 1×10^{-9} seconds, (Barrow, 28).
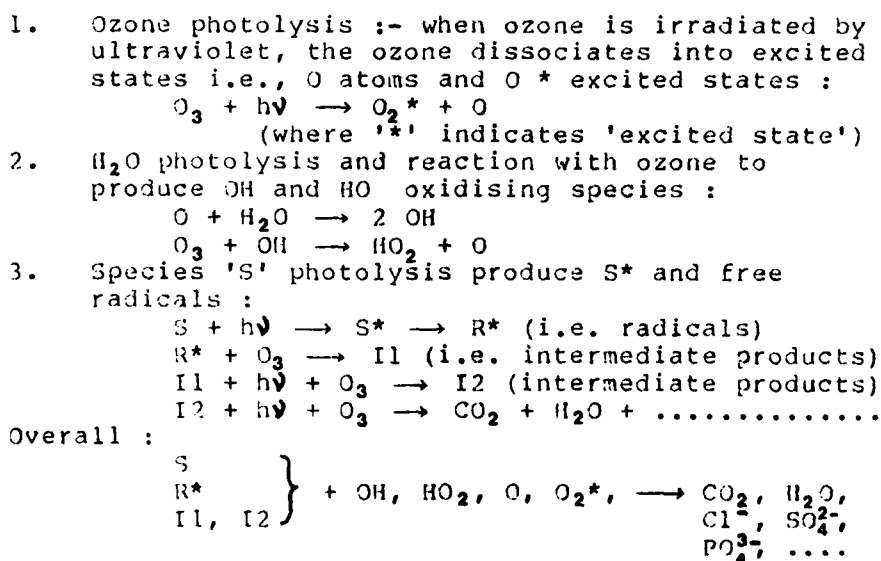
Because of the low bond strength of ozone and its large absorption coefficient in the U.V. range, one would expect a photochemical change to occur. The first two absorption bands for ozone are shown in Fig.4, (Calvert & Pitts, 29).

Fig. 4 :
Absorption
Spectrum
of
Ozone.
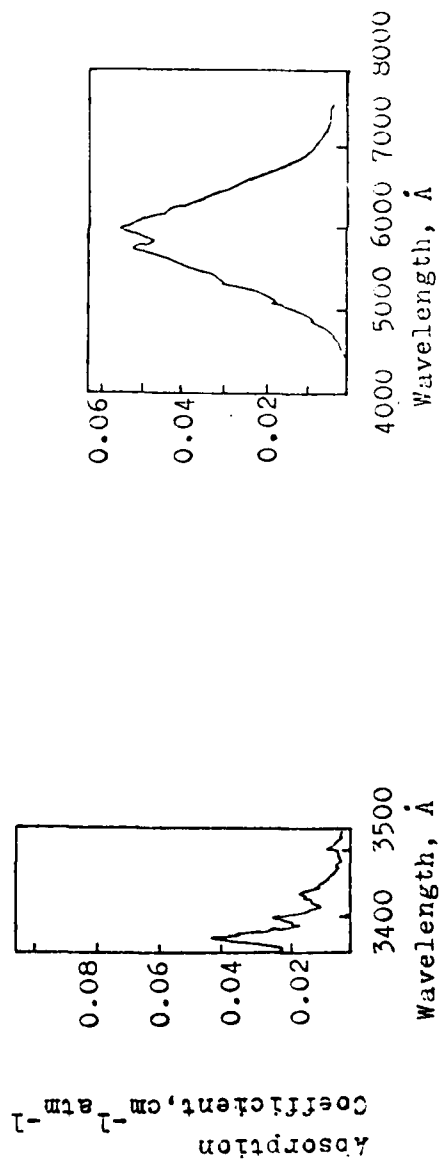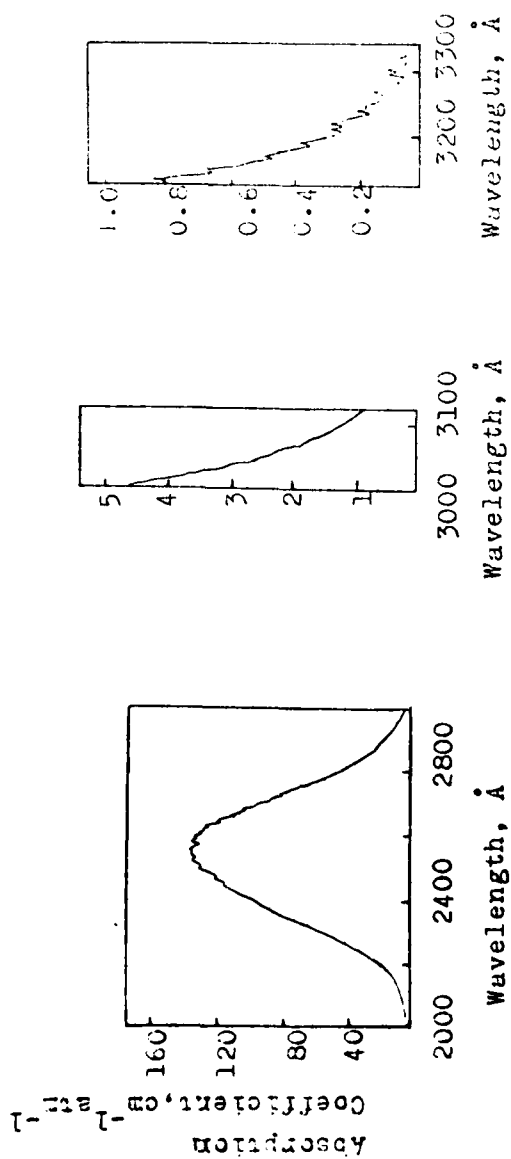
Ultraviolet radiation appears to enhance the oxidation of organic molecules via two stages. First, ultraviolet energy decomposes ozone molecules to reactive oxygen atoms and diatomic oxygen. These, along with intact ozone molecules, attack the organic species present and oxidise them. Secondly, ultraviolet energy activates some organic species, thus rendering them more susceptible to oxidation. Excitation of the molecules occur and free radicals are produced which are very reactive in the presence of ozone. The wavelengths of the ultraviolet radiation suitable for ozone/U.V. oxidation is 180-400 nm. At this wavelength, the radiation provides sufficient energy (72-155 kcals/mole), (30), for producing substantially more free radicals, as well as excited-state species both from the initial compound and subsequent intermediate products. Such excited-state species are not produced by ozonolysis alone.

Hence excited atomic species (O), hydroxyl (OH) and hydroperoxyl (HO_2) radicals, and excited-state species (S*) are produced from the reactant molecules. These radicals initiate many more propagation chains. The result is an increase in the oxidation rate and also the possibility of complete oxidation without plateauing. Therefore, the use of ultraviolet energy greatly enhances oxidation rates over the rates obtained as a result of ozonolysis alone. The chemistry involved in the ozone/U.V. photochemical excitation/oxidation of a molecule (species 'S', say) in aqueous solution is shown below :

1. Ozone photolysis :- when ozone is irradiated by ultraviolet, the ozone dissociates into excited states i.e., O atoms and O * excited states :
$$O_3 + h\nu \longrightarrow O_2^* + O$$
(where '*' indicates 'excited state')

2. H_2O photolysis and reaction with ozone to produce OH and HO oxidising species :
$$O + H_2O \longrightarrow 2\ OH$$
$$O_3 + OH \longrightarrow HO_2 + O$$

3. Species 'S' photolysis produce S* and free radicals :
$$S + h\nu \longrightarrow S^* \longrightarrow R^* \text{ (i.e. radicals)}$$
$$R^* + O_3 \longrightarrow I1 \text{ (i.e. intermediate products)}$$
$$I1 + h\nu + O_3 \longrightarrow I2 \text{ (intermediate products)}$$
$$I2 + h\nu + O_3 \longrightarrow CO_2 + H_2O + \ldots\ldots\ldots\ldots$$

Overall :
$$\left.\begin{array}{l} S \\ R^* \\ I1,\ I2 \end{array}\right\} + OH,\ HO_2,\ O,\ O_2^*,\ \longrightarrow CO_2,\ H_2O, \\ Cl^-,\ SO_4^{2-}, \\ PO_4^{3-},\ \ldots$$

The power of the oxidising species is listed in Table 1.

Table 1 : Comparison of Oxidation Potential of Ozone
and its Photolysis Species,
and other common oxidants. (31)

Species	Oxidation Potential (Volts)	Relative * Oxidation Power
Fluorine, F_2	3.06	2.25
Hydroxyl Radical, OH	2.80	2.05
Atomic Oxygen, O	2.42	1.78
Ozone, O_3	2.07	1.52
Hydrogen Peroxide, H_2O_2	1.77	1.30
Perhydroxyl Radicals, HO_2	1.70	1.25
Hypochlorous Acid, HOCl	1.49	1.10
Chlorine, Cl_2	1.36	1.00

* :- Based on chlorine as a reference.

5.2 OXIDATION OF REFRACTORY COMPOUNDS

A refractory compound generally is regarded as being resistant to conventional treatment processes. Prengle, et al., (?0) defined a 'Refractory Index', (RFI) for the comparison of different refractory species. The refractory index is a measure of the difficulty of oxidation of a given molecular species. Organic acids, acetic and oxalic, produced as end products of bio-oxidation of aliphatic and aromatic compounds, are very highly refractory.

Ozonolysis of organic solutions results in organic oxidation and hydroxyl radical formation. The ozone attacks the carbon-carbon double bonds to form unstable ozonides which decomposes into smaller oxidation species until either carbon dioxide (CO_2) and water (H_2O) , or stable unoxidisable (refractory) compounds such as acetic acid and oxalic acid , are formed. The latter causes the oxidation to plateau at some equilibrium level, resulting in incomplete oxidation. Hence, for refractory type species, oxidation by ozone alone is relatively slow. The overall process is reaction rate controlled and hence the ozone is not fully utilised. With ultraviolet, excitation of the molecules occurs and more free

radicals are produced which are highly reactive in the presence of ozone. The ultraviolet radiation activates both the ozone and the organic species.

Trace organics were destroyed much more rapidly by UV-ozone than by either UV or ozone alone, in a study on the development of UV-ozone systems for the Army and for NASA manned spacecraft, (27). Prengle ,et al., (30) found that in the absence of ultraviolet radiation, acetic acid is essentially unoxidised by ozone. With ultraviolet radiation, the oxidation proceeds rapidly at room temperature, and in fact, moves the rate from the reaction controlled to the mass transfered controlled regime. Elevated temperature and higher ozone concentration also enhances the oxidation rate but neither of these appears to be as effective as additional ultraviolet radiation.

Considerable interest is currently focussed on the need to eliminate halogenated hydrocarbon contaminants from source water. These compounds show remarkable persistence and may, in some cases, be potential carcinogens or carcinogen precursors. Oxyphotolysis is very effective for oxidation of chlorinated compounds in water, resulting in stable products such as Cl_2 , Cl^- , CO_2 and H_2O. Recent E.P.A. (U.S. Environmental Protection Agency) sponsored studies (32) have shown that ozone/UV can reduce the levels of polychlorinated biphenyls (PCB's) in industrial wastewaters to less than 0.01 micro g/l. Activated carbon adsorption can only reduce PCB levels to 0.1 micro g/l. The proven ability of ozone/UV combinations to very rapidly destroy refractory compounds which are normally quite oxidation resistant, such as PCB's, must be considered by industries when evaluating techniques for reducing T.O.C. concentrations and for certain toxic substances. The process is particularly effective with refractory compounds such as phenols, acids, amino acids, and fatty acids. The process is ideal for treating toxic and potentially toxic (when chlorinated) impurities as a tertiary process.

6   HYDRODYNAMICS OF LIQUID FILMS ON A ROTATING DISC

A lot of information is available on the hydrodynamics controlling the flow of liquid films formed under the action of gravity on vertical and inclined stationary planes.   Such thin films present a large area for mass transfer.   Also, due to the presence of a wave motion (ripples), which is a characteristic of such films, the rates of heat and mass transfer is increased.   This is caused by the turbulence due to the interfacial waves and by an increase in the interfacial area of the film.   Hence the internal resistance to heat and mass transfer is minimised.

Liquid films produced by centrifugal forces on surfaces rotating horizontally can be controlled more effectively than those formed under the action of gravity on stationary planes.   The parameters governing the hydrodynamics of liquid films flowing across a rotating disc are film thickness, surface waves, surface velocity and velocity profile. Various models have been proposed by different investigators to describe the flow of a Newtonian fluid on a rotating disc. Various methods of measuring the thickness of the film were used by different investigators.

6.1   MASS TRANSFER INTO THIN LIQUID FILMS

As a liquid film flows down a vertical plane, its free surface is nearly always disturbed by wave motions and ripples.   Many investigators have also found that experimemtal mass transfer rates were greater than theoretical prediction based on a true molecular diffusion in a perfect laminar liquid film.

Portalski (33) suggested that the increase in experimental mass transfer rate may be due to a combination of two effects :

1.   the efficient bulk mixing due to rippling, and

2.   the increase   in the interfacial area caused by the wave motion.

Fulford (34) suggested that it is the enhanced bulk mixing action of the ripples at the free surface that causes the higher mass transfer rate rather than an increase of the interfacial area, since Bruaer (35) has shown that the increase in interfacial area does not exceed 3 %.

Investigating the mass transfer to liquid films on an inclined plane, Oliver and Atherinos (36) found that the mass transfer coefficients increased with increased angle of inclination. The greatest deviation from the smooth film theory occurred when the plane is vertical. They concluded that the increase in the mass transfer coefficients was due to the occurrence of rippling as the slope increases. Also, as the slope becomes steeper, the wave velocity increases and the wavelength decreases. Sherwood and Pigford (37) found that at high Reynold's number, there is a wide deviation between the experimental and theoretical transfer rates. Brauer (38) has shown that the experimental results may be as much as three times higher.

Lim (39) studied the mass transfer of oxygen into thin liquid films formed on a 36 cm diameter rotating disc and showed that the measured values of mass transfer rate are much higher than those predicted from a theoretical model based on a laminar flow regime within the film and a smooth interface. He also showed that the increase in interfacial area due to wave motion is insignificant to account for the increase in the rate of mass transfer. Hence it is most likely that efficient bulk mixing due to wave motion and the rippling causes the increase in absorption rates.

By monitoring the concentrations of dissolved oxygen on and after the disc, it was found that at low disc speed, the mass transfer to the liquid spray at the edge of the disc represents a significant contribution to the total oxygen transfer to the liquid. The contribution to mass transfer provided by the spray increases with increasing flowrate up to rotary speeds of about 600 rpm, after which, the total mass transfered to the liquid (i.e. both on the disc surface and to the spray) remains virtually the same. Hence at rotary speeds in excess of 600 rpm, the mass transfer on the disc surface becomes progressively dominating. For example, at a flowrate of 40 cc/s and rotational speeds of 600 rpm, about 80 % of the total mass transfered is already achieved on the disc. Any further increase in rotational speed will only further increase the contribution to mass transfer on the disc without any major increase to the total mass transfered. At a disc speed of 1110 rpm, the liquid is virtually saturated when it reaches the edge of the disc for all flowrates less than 40 cc/s.

As the flowrate is increased, the mass transfer coefficient increases to a maximum value at flowrates in the range 30 - 40 cc/s and then decreases with further increase in flowrates. As the disc speed is increased the maximum

occurs at higher flowrates. These phenomena are most probably due to the mixing mechanism in the film. As the flowrate increases the film thickness increases. This enables the waves to induce progressively more efficient mixing in the film. However beyond an optimum film thickness, the waves are unable to exert the higher levels of mixing required to produce the higher mass transfer rates. This causes a reduction in the mass transfer coefficient with any further increase in flowrates at a particular rotational speed. Lim (39) defined a function :

$$E = \frac{C_{out} - C_{in}}{C^* - C_{in}} \qquad \ldots\ldots(6.1)$$

where E = fractional approach to equilb.
C^* = saturation concentration
C_{out} = conc, at a particular radius
C_{in} = inlet concentration

and correlated it with parameters associated with the hydrodynamics of liquid films on a rotating disc :

$$E = f(Re, Ta, R^*) \qquad \ldots\ldots(6.2)$$

where Re = $Q/(r v)$
Ta = $(r w^2)/v$
R^* = r/r_i

The range of variables investigated was :

$$30 < Re < 1030$$
$$8 \times 10^4 < Ta < 4 \times 10^6$$
$$2.67 < R^* < 8.0$$

A least squares fit produced a simple equation by which the performance of the disc could be assessed :

$$E = 6.17 \times 10^{-3} Re^{0.46} Ta^{0.51} R^{*-0.05} \qquad \ldots\ldots(6.3)$$

where Re = $Q/(r v)$
Ta = $(r w^2)/v$
R^* = r/r_i

All these data were also correlated with Sherwood Number, Sh = $(K_L)/D$, resulting in :

$$Sh = 4.76 \times 10^{-3} Re^{0.68} Ta^{0.37} R^{*-0.53} \qquad \ldots\ldots(6.4)$$

It should be noted that these two correlations contain only those data for which E was less than 0.95. Although these equations were derived from the study of absorption of oxygen into water films, they are probably valid for any other physical absorption process in a rotating disc contactor.

7   CONTACTOR DESIGN FOR THE OZONATION PROCESSES

Ozone is relatively insoluble in water and hence considerable attention has to be directed towards the most effective methods of bringing the gas into intimate contact with the water so that maximum absorption may be achieved and the wastage of ozone shall be reduced to a minimum. The process of oxidising water soluble material can be limited either by mass transfer of the ozone into the water or by the reaction kinetics of the ozone-aqueous system. The reaction mechanism of ozone varies with the organic species with which it reacts. Reaction rates of such materials as bacteria, nitrites, hydrogen sulphide, unsaturated compounds, etc., are limited only by mass transfer. On the other hand, refractory materials react with ozone very slowly, eg., urea, acetic acid, etc., even in the presence of a relatively high concentration of ozone; these reactions are 'reaction rate limited'. The type of ozone application determines the requirements placed on the ozone contactor. Hence, one of the objectives of this research is to evaluate the performance of the rotating disc contactor for ozonolysis of effluents.

7.1   MECHANICAL DESIGN OF THE SPINNING DISC REACTOR

7.1.1   The Disc Assembly

The disc was constructed out of aluminium for lightness, corrosion resistance to ozone and water, and amenability to a smooth surface finishing. The diameter of the disc should not be too large so as to avoid the difficulties encountered in the design of a large 'balanced' disc. On the other hand, a disc with too small a diameter would involve the 'entrance effect' playing an important role in the fluid dynamics of the liquid film on the disc. Hence a 33 cm disc was used.

To have an entirely smooth top surface, the disc was mounted on to a disc support plate from below. The latter was bolted to the liquid distributor head. The screw threads on the rotating assembly (liquid distributor head, rotating central shaft, rotary union) are all designed so that with the designed sense of rotation (clockwise looking vertically downwards) all screws are tightened by inertial loads.

7.1.2　The Liquid Feed Distributor

The liquid feed distributor comprises of the following parts :

1. Distributor head with distributor plate.

2. Rotating central shaft.

3. Housing for securing the central shaft.

Two main factors dictated the design of the liquid feed distributor at the centre of the disc :

1. ability to spread the liquid uniformly on the surface of the disc without jetting of the liquid on the rotating disc.

2. to minimise the inertial and Coriolis effects, the liquid has to be introduced at the disc's rotational speed.

The distributor plate prevents the jetting of the liquid as it emerges from the holes of the rotating distributor head. The distributor gap (i.e. the gap between the disc surface and the distributor plate) can be adjusted by means of spacers. The bottom end of the shaft is threaded internally to accept the rotary union (Model 55-003 by Deublin Company). The entire liquid feed distributor unit was made out of stainless steel. Oil seals and 'O'-ring seals used in the central shaft housing and elsewhere in the reactor were of Viton material.

7.1.3　The Reactor Chamber

The reactor chamber was constructed out of stainless steel. The cover of the reactor was made out of acrylic sheet. Liquid is introduced onto the disc at the axis of rotation through the holes of the distributor head via the core of the rotating shaft. This is to ensure that the liquid is being introduced at the same rotational speed as the disc. The liquid spraying off the edge of the disc collects in the annulus formed by the wall of the chamber housing the disc and a strip of metal sheet (liquid barrier) welded onto the base of the reactor chamber so as to leave a circular annulus of 140 mm width. The liquid flows by gravity through an outlet hole into the holding container (reservoir).
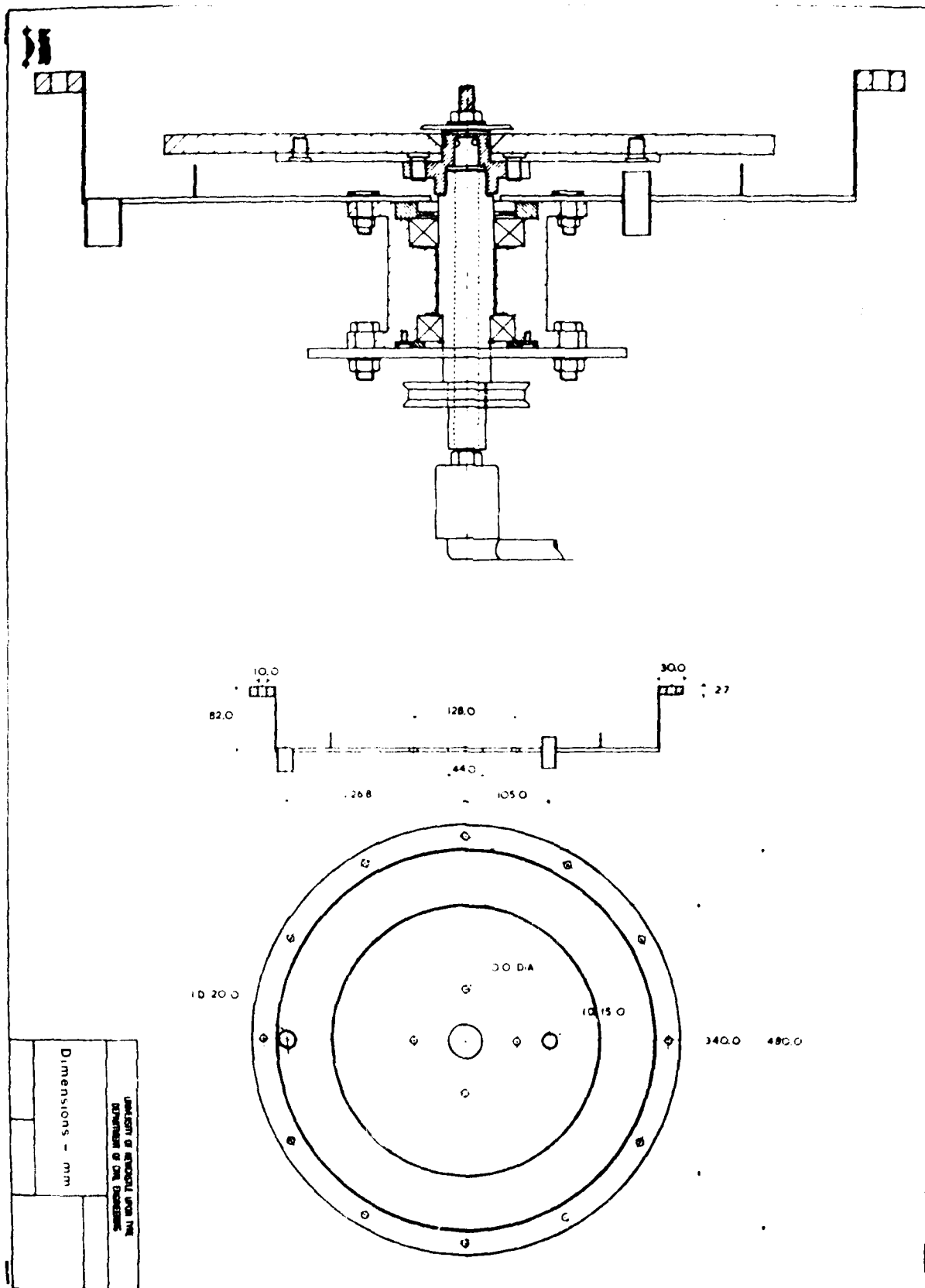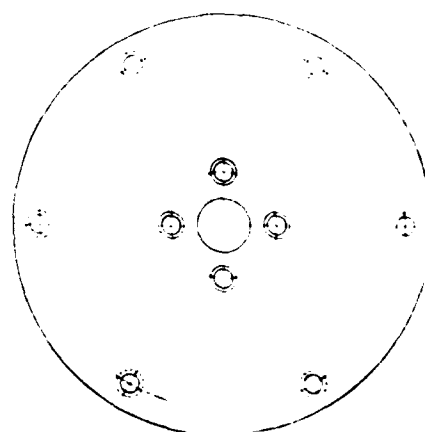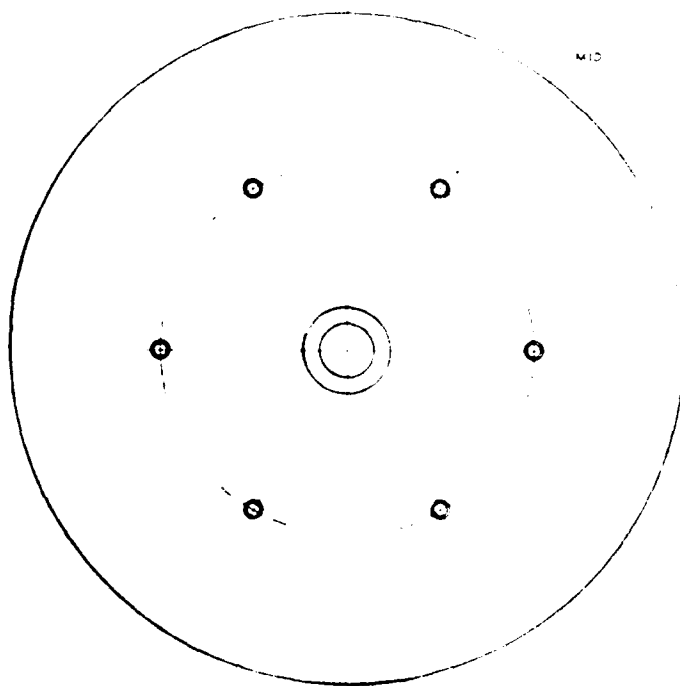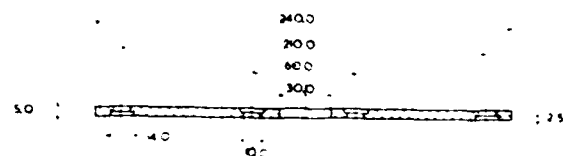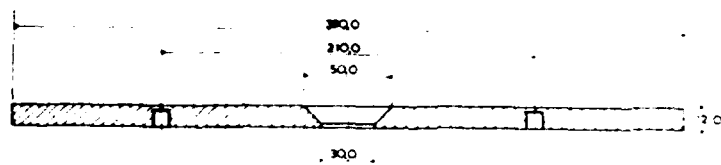
PLATE 2 - THE ROTATING DISC CONTACTOR

PLATE 3 - LIQUID FEED DISTRIBUTOR UNIT

Dimensions - mm

PLATE - THE DISC ASSEMBLY

7.1.4 The Drive and the Structural Supports

A 3-phase 1.5 Hp motor capable of a maximum speed of 1400 rpm was used. A variable gear box was coupled to the motor shaft. The disc was driven by the motor via a 'Vee' belt (SPZ 1010, Fenner Alpha 400) and pulleys (No. Fenner 160 SPZ). The pulley's diameter ratio for the motor and the spiral-T shaft was 1:2. This enable the speed to be varied between 230 rpm to 1120 rpm. Two structural supports were constructed; one for the motor, variable gear box and housing for the spiral-T gear unit, and the other for the rotating disc reactor itself.

7.1.5 Design of the Quartz Photochemical Reactor

Plate (5) shows the photochemical reactor and ultra-violet source used in this work. The quartz photochemical reactor has been designed such that it is efficient for photochemical reactions since the ultra-violet lamp itself is effectively surrounded by the solution to be irradiated. It is a double-walled flow-through reactor. The inner well houses the irradiation lamp. A small diameter inlet tube extends to the bottom of the inner quartz tube housing the lamp, to allow cooling gas (if necessary) to pass from the bottom of the well upwards.
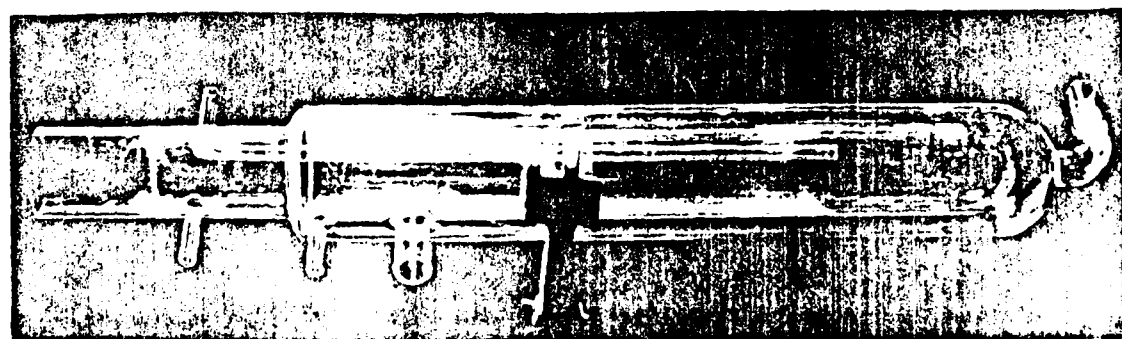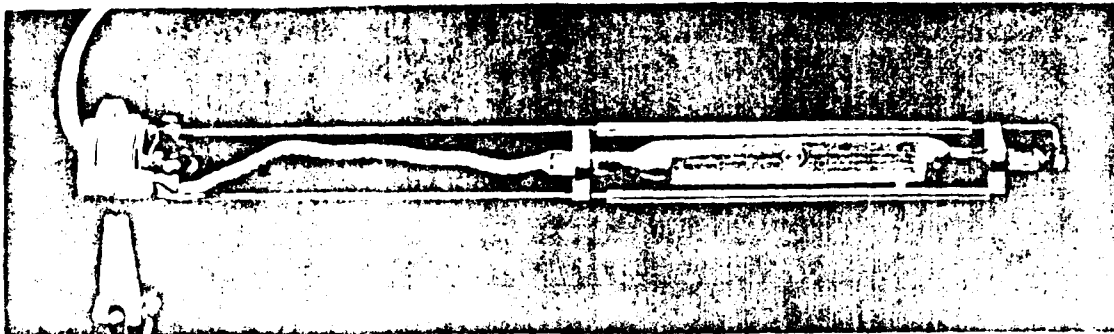
PLATE 5 - THE QUARTZ PHOTOCHEMICAL REACTOR AND U.V. LAMP

8   EXPERIMENTAL

8.1   DESCRIPTION OF EXPERIMENTAL LAYOUT

The ozonator used in this work was a Wallace and Tiernan, Model BA-023. It consists of a single vertical discharge tube mounted in a sealed metal jacket, a high voltage transformer, a rotary regavolt and a variable-area flowmeter. All are built into a metal cabinet. The high tension transformer is supplied at 240 V, AC and yields a maximum of 5000 volts at the secondary winding. The rotary regavolt is connected in the circuit to the primary winding of the transformer to provide for adjustment of the voltage applied to the ozone discharge tube. The the ozonator is always calibrated at the beginning and end of each run, throughout the course of this research. It operates on a feed of either air or oxygen. The gas flows through a silica gel dryer/filter, through rotameters R1 or R2 before entering the ozoniser. Maximum output from the ozonator is not attained until a dew point of minus 50 $^{\circ}$C is reached. A Shaw Hygrometer was used to monitor the humidity of the feed gas after it leaves the silica gel dryer. Dust particles were filtered from the air or oxygen supply using glass wool, a material which has little tendency to absorb moisture. It is important to remove dust particles because it may lodge at the glass discharge valve or the glass dielectric and hence impair its efficiency.

The outlet ozone stream from the ozoniser can be directed into any of three paths (Fig.5). Firstly it can be directed straight to a series of two 250 ml. gas-absorption bottles (Dreschel bottles) each containing 150 ml. of 2 % potassium iodide solution. This is to monitor the inlet concentration of the ozone used for a particular run. Secondly the flow may be directed to a 20-litre glass CSTR (continuous stirred tank reactor) which also acts as a reservoir for the liquid to be treated. Finally the flow may be directed to the chamber housing the rotating disc (i.e. the rotating disc reactor). The outlet gas stream from either the rotating disc reactor or from the reservoir is then passed through a series of two 250 ml. gas-washing bottles to measure the concentration of any remaining ozone. Upon exiting the absorption bottles, the gas was passed through a wet gas meter to correlate readings of the rotameter and then expelled to the atmosphere.

The rotating disc reactor can be operated as a one-pass continuous flow reactor or as a semi-batch reactor (i.e.

closed loop) so as to enable control of the overall residence time. Hence the rotating disc reactor is connected to a holding tank, which is either the 20-litre glass isothermal vessel, or if a larger volume is required, a number of 40-litre cylinders. For a batch run, liquid is pumped from the holding tank, via rotameters, to the rotary union, up the core of the rotating shaft and onto the rotating disc. The flowrate through the system was monitored by rotameters and manually controlled. The reacted liquid emerges from the outlet of the rotating disc reactor, passes through the photochemical reactor (optional, depending on which run), back into the reservoir and is then recycled. For a one-pass continuous run, the liquid outlet goes to the drain instead of the reservoir.
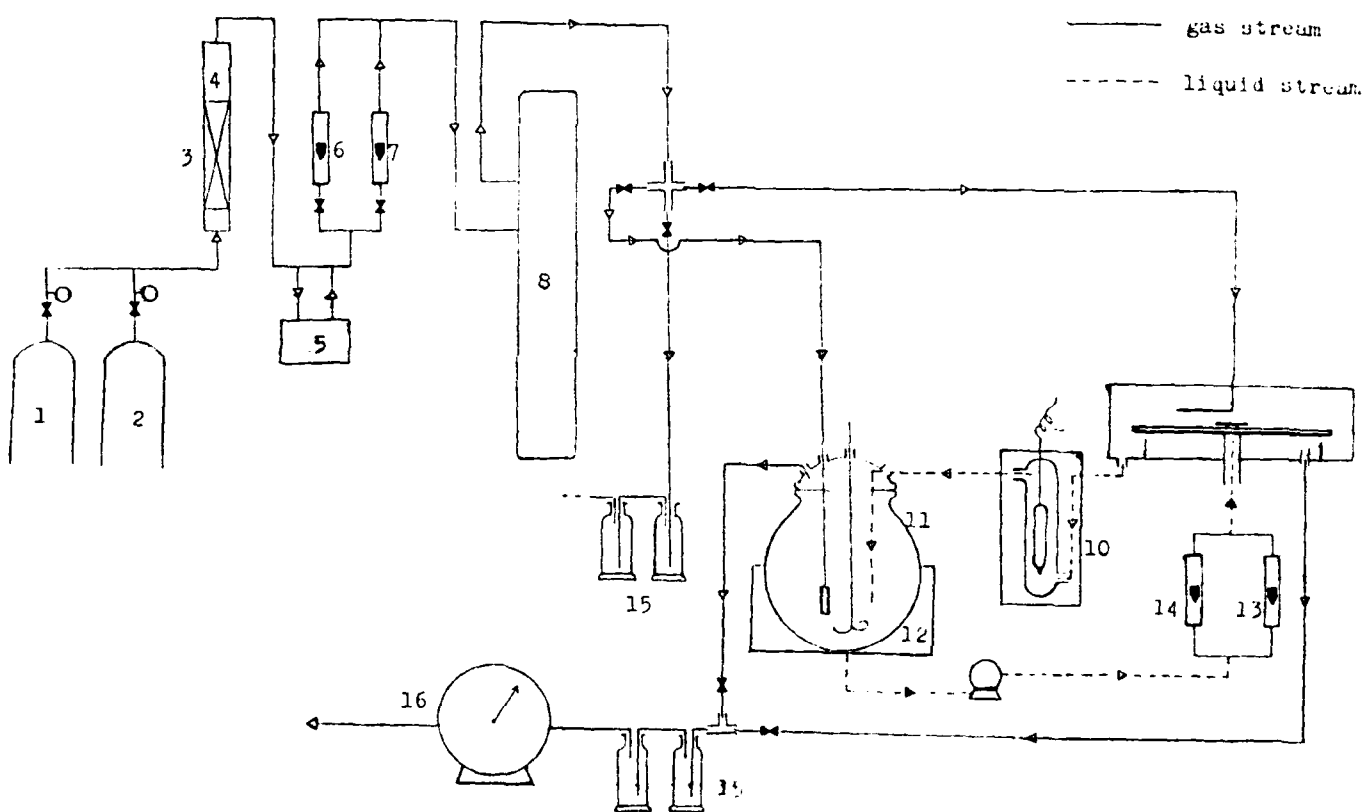
gas stream

------- liquid stream

Fig. 5 : Process Flow Diagram

Process Flow Diagram

1. Air cylinder.
2. Oxygen cylinder.
3. Silica gel dryer.
4. Glass wool filter.
5. Shaw Hygrometer.
6. Rotameter R1.
7. Rotameter R2.
8. Ozoniser.
9. Rotating Disc Reactor.
10. Quartz Photochemical Reactor immersed in water bath.
11. 20-litre Quickfit vessel.
12. Electrothermal heating mantle.
13. Rotameter L1.
14. Rotameter L2.
15. Gas-Washing bottles.
16. Wet-gas meter.
17. U.V. power supply.
18. Digital voltmeter.
19. Tachogenerator and thermocouple connections.
20. Avometers.
21. Graph plotter.
22. pH meter.
23. Oxygen meter.
24. Oxygen meter sensor.
25. Electrothermal Energy Controller.
26. 3-phase 1.5h.p. motor.
27. Gear Unit.
28. Paper Tape puncher.
29. Solatron Digital Voltmeter.
30. Solatron 7055 microprocessor Voltmeter.
31. Solatron-Schlumberger Data Transfer Unit.
32. Stroscope unit.
33. Sangamo Weston wattmeters.
34. Immersion heater.
35. Immersion heater temperature controllers.
36. Constant temperature baths.
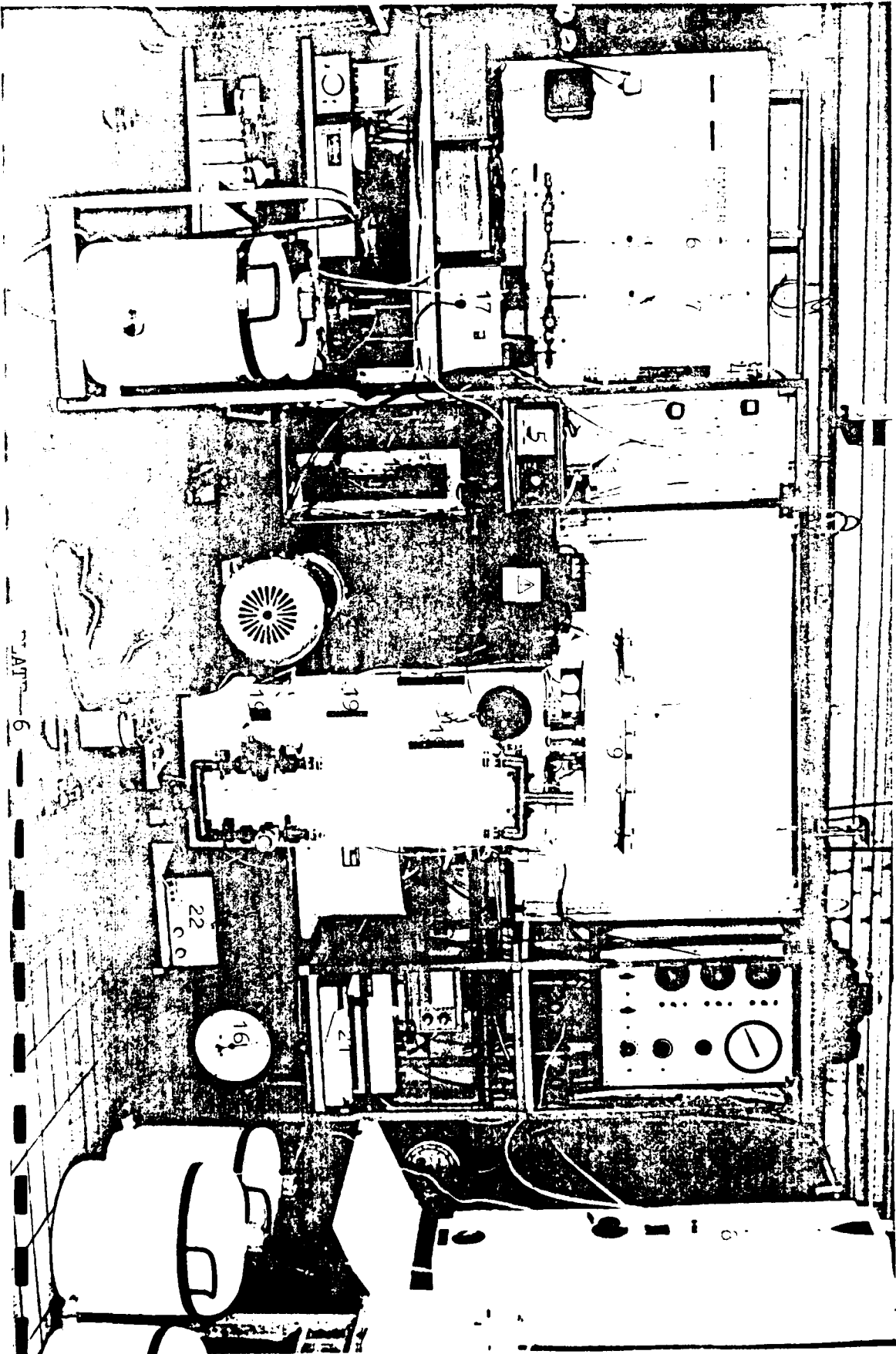
8.2   MATERIALS OF CONSTRUCTION

Special materials are required principally for parts in contact with ozone. Copper and brasses, while not attacked by the dry gas, show rapid corrosion in the presence of moist ozone. Natural rubbers show rapid disintegration. Polyurethane was not used because of possible failure when exposed to ultra-violet light.

Hence stainless steel, aluminium and Tygon were used for tubing and fittings in contact with ozone. Polythene and polypropylene appear to be completely resistant as does PTFE. Glass is also completely resistant. All valves used were of ozone-resistant materials. Synthetic rubbers (Viton and silicon) were used for parts in contact with ozone (eg., 'O' rings). Viton is extremely resistant to corrosive chemicals, ozone and to ageing as well. It has excellent mechanical properties.

8.3   INSTRUMENTATION

1.   Electrical control equipment and instrumentation :

   a.   Voltage regulation via transformers :- for ozone production control, special characteristic transformers with primary circuit tappings to vary the high tension applied to the electrode system were incorporated in the ozone generator.

   b.   Switching :- the necessary contactor and circuit-breaking equipment for all electrically operated units gave means of control and protection actuated through relays and push-buttons.

   c.   Measuring instruments :- voltmeters and ammeters were of standard types. Weston wattmeters (Sangamo Weston Ltd.) were used for measuring the power consumed by the 3-phase 1.5-h.p. motor, with and without liquid flowing on the disc.

   d.   Cables :- low and high tension cables were of standard types.

2.   Measurement of flow :- Liquid rotameters were used for controlling the flow of liquid into the contactor. Gas rotameters and a wet gas meter were used to monitor the flow of the gas stream.
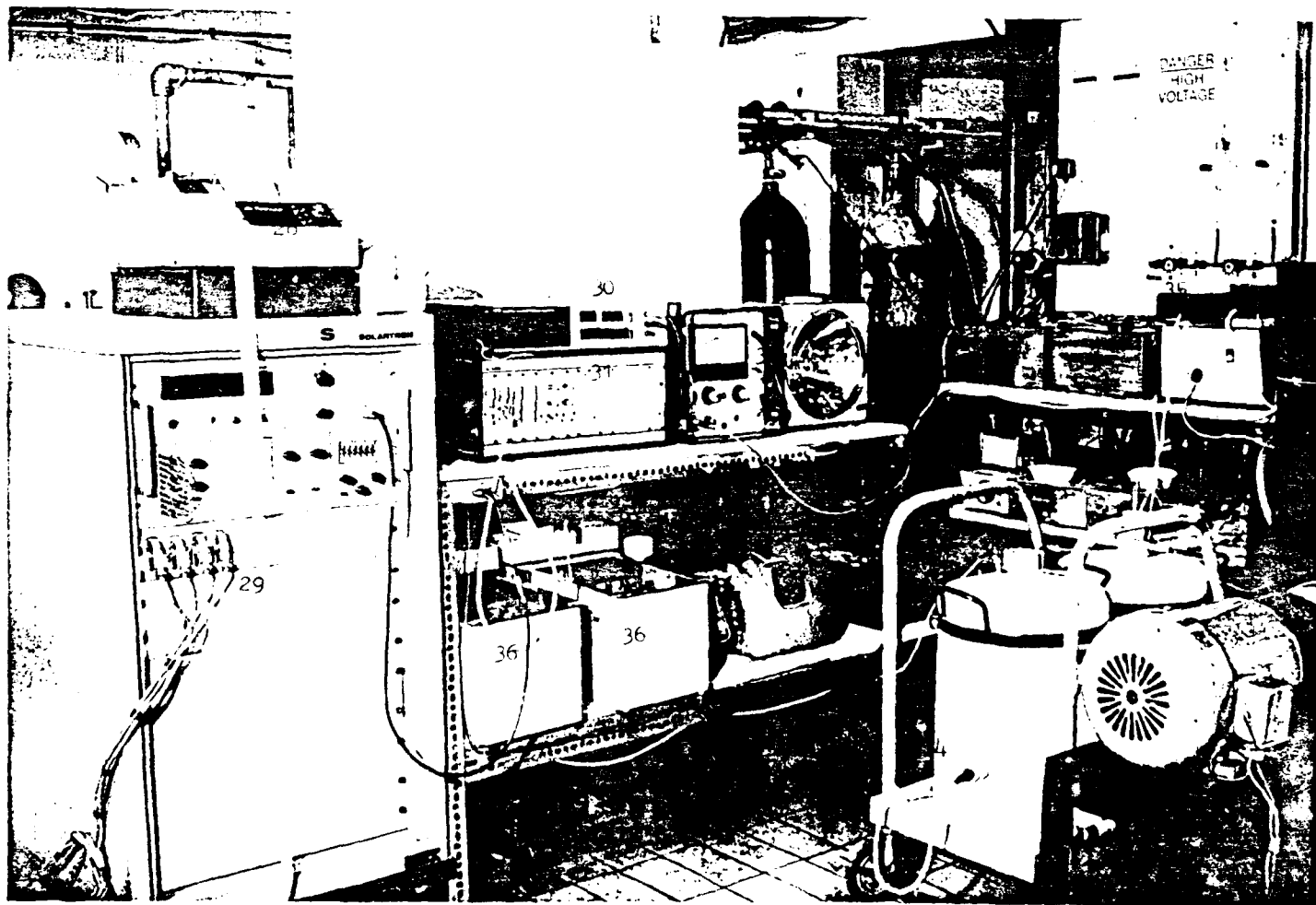
3. Measurement of temperature :- Automatic temperature control (electrical immersion heaters with temperature controllers) were used to achieve a desired temperature for the liquid stream. Standard copper-constantan thermocouple wires (36 SWG by Saxonia Company Limited) were used to monitor the temperature of the air and liquid stream. The 20-litre glass reservoir (Quickfit & Quartz Ltd., Type 2/1406/A) sits on an electric heating mantle (Electrothermal, Cat. No. M110/S311). The mantle has three separate heating circuit which can be operated independently e.g., when dealing with small volumes of liquid, lower circuits only need to be used. Thermocouples for indicating the surface temperature of the element are built into the heating mantle and these temperatures are indicated on the Electrothermal energy controller unit.

4. Measurement of humidity :- A Shaw Hygrometer was used to measure the humidity of the air leaving the dryer.

5. Measurement of pH :- The pH was monitored by means of a WPA Saffron Walden pH Meter.

6. Measurement of oxygen content :- A Beckman Model 715 Process Oxygen Monitor was used to monitor the oxygen content of the liquid stream.

7. Measurement of pressure :- Pressure indicators were used to monitor the pressure of the air preparation system.

8. Measurement of rotational speed :- A tachogenerator (Muirhead Ltd.) was used to measure the rotational speed of the rotating disc. It was fitted to the shaft of the spiral-T gear unit. The readings were recorded on a DVM (digital volt meter), and also registered on paper-tape via a data-logger.

9. Visual examination of formation of waves on the disc :- A stroboscope (Strobosun Type 1203C) was used for visual examination of the formation of waves (ripples) and to ensure that there is no film breakdown on the disc.

To ensure that the whole system is operating isothermally, thermocouples were used to monitor the temperature of the liquid stream at various points. The output of all these thermocouples were logged on paper tape via a Solartron-Schlumberger analogue scanner, data transfer unit and digital volt meter. Means of maintaining an isothermal condition throughout the whole system includes adjustments to the electrical heater in the sample reservoir, adjustments to

the electrical immersion heater in the photochemical reactor
water bath, adjustments to the flow of cooling gas through
the photochemical reactor and adjustments to the electrical
heating coil wound round the outside of the rotating disc
reactor chamber. This heating coil wound round the reactor
chamber helps to maintain the gas at the same temperature as
the liquid. This also helps to prevent vaporisation of the
liquid film into the gas phase in the reactor, which in turn
helps to minimise the gas phase resistance to mass transfer.

It was found that it is possible to maintain a desired
temperature throughout the whole system by manipulating these
parameters. The data logger is particularly useful for
scanning all these temperature measurements and for scanning
other measurements as well (eg., the rotational speed of the
rotating disc).

8.4 SOURCES OF SAMPLES

The multicomponent samples used for this research were
obtained from a local Waste Treatment Works. This is an
activated sludge plant that treats mixed domestic and
industrial wastes. The main processes comprise :

1. Screening and disintegration.

2. Grit removal.

3. Primary settlement.

4. Activated sludge plant.

5. Final Settlement.

6. Discharge of effluent to river.

7. Sludge treatment and removal.

The discharge of 'trade effluents' from the local factories
account for about half of the works load. Because of the
varied, complexed and often toxic nature of industrial
effluent a comprehensive monitoring of these effluents and
their effect on the works must be maintained. In this
locality, there are effluents as diverse as electroplating,
dyeing, cyanide hardening, etching, pharmaceutical process
waters and cooling waters.

The 'AVERAGE' discharge conditions from this treatment
plant are shown in Table 2. It must be pointed out that
these are just 'averaged range' and the actual values of each
of the water quality parameter varies from day to day.

On occasion, highly coloured wastes (from textile
industries) are present and, because of the refractory nature
of the dye, these samples were used to investigate the effect
of ozone and U.V. The single component effluent used in this
study was phenol, chosen because it has been observed in
recycled drinking water in low concentrations.

Table 2 :   Waste water characteristics of Cramlington Effluents

Parameters	Raw Sewage	After Primary Clarifier (settled)	After Secondary Clarifier (settled)
BOD mg/l	300-350	200-300	30-50
			60-90 (highly coloured wastes)
COD mg/l	800-1200	700-1000	230-260
Suspended Solids (mg/l)	200-300	130-150	40-80
Colour (H)	300-400	250-300	100-150
	500-900	400-700	300-350 (highly coloured)

The Royal Commission Standard stipulates that the conditions for discharge to receiving water with available dilution of 8 to 1 should be :

$$BOD - < 20 \ mg/l$$
$$S. \ Solids \ - < 30 \ mg/l$$

8.5   OPERATION PROCEDURES

The ozonator was fed by either air or oxygen. The feed
pressure was maintained at 8 psig, stabilised with two
flostats before passing through the two gas rotameters. The
ozone output and concentration was adjusted by means of the
rotary regavolt and needle valve controlling the air or
oxygen supply. The concentration of the ozone stream was
monitored by absorbing the gas in a series of potassium
iodide traps.

After ascertaining the desired ozone concentration in the
ozone stream, the flow was directed to the rotating disc
reactor chamber. During this period the disc was kept
rotating at a speed of 600 rpm. The outlet gas stream from
the chamber was directed to a series of gas-washing bottles
containing potassium iodide solution. After steady state
concentration was attained, the liquid was pumped from the
reservoir, via the rotameters and the stationary rotary
union, up the rotating shaft and on to the rotating disc.
The liquid from the outlet of the reactor goes back to the
reservoir. The liquid is then recycled. Samples were
withdrawn from the reservoir for analysis. In consistent
with our aim of evaluating the performance of the rotating
disc reactor of this particular dimensions at its optimum
conditions (Section 6.1), most of the runs were performed at
a liquid flowrate of 30 cc/s, a rotatonal speed of 600 rpm,
and a gas flowrate of 40 litre/hour. The distributor gap was
set at 0.03 inches (0.76 mm) in accordance with Bell's (40)
gap-thickness correlation which ensured that liquid entered
onto the disc smoothly.

Liquid and gas flow rates and treatment time were noted to
determine the ozone application rates. Samples were taken at
regular time intervals. When calculating ozone dosages,
compensation for the loss of liquid due to sampling was taken
into account. The ozone dosage levels calculated represent
the actual amount of ozone consumed by the treatment.

8.6   ANALYTICAL PROBLEMS WITH OZONE

One of the main problems of measurement of ozone both in
the air and water is contamination. We are generally
measuring ozone in the presence of other things.
Problems of measurement of ozone in the gas phase :

1.   Presence of water vapour.

2.   Effect of temperature on measurement.

3. Gases in the waste treatment system such as carbon dioxide and other oxidation products of ozonation.

4. Gases stripped while treating water, such as nitrogen and other volatile matter.

Problems of measurement of ozone in the liquid phase :

1. Other oxidants could be present or might actually be formed during ozonation.

2. The determination of ozone in water solution is complicated by the instability of the ozone in solution. It decomposes readily. Hence the effect of time delay with respect to the measurement being made is considerable.

3. Ozone loss from aqueous solution to atmosphere above the solution.

All the above factors affect the precision and accuracy of the calibration and analysis procedures. For our purpose, it was found that the neutral unbuffered potassium iodide method gave the most reliable and accurate result. Throughout the experiment, all chemicals used were of reagent grade, and titration measurements were carried out immediately after sampling. Because of the great reactivity of ozone, all the laboratory apparatus were kept very clean.

8.7   MASS TRANSFER STUDIES

Because of the low solubility of ozone in aqueous solutions, mass transfer studies are of great importance in the design of an efficient contacting system. The following factors were studied in order to assess the performance of the rotating disc reactor :

1. rate of transfer of ozone into the water.

2. its distribution coefficient, (i.e., solubility ratio).

3. mass transfer coefficient of ozone in water.

In addition, the effects of pH on the rate of decomposition of ozone in water were also studied.

8.7.1 Determination of Ozone Concentration in the Gas Phase

Ozone analysis were performed on the feed and exit gases during each run. The gas was passed through a series of two absorption bottles each containing 150 ml. of 2 % neutral potassium iodide solution. Actually, during each time interval, the first bottle was already sufficient to trap all the ozone, as revealed by sample analysis of the solution in the second bottle. The solution was acidified with 10 ml. of 2 % sulphuric acid and titrated against 0.1 N sodium thiosulphate solution using 5 ml. of 0.5 % starch as indicator.

8.7.2 Determination of Ozone Concentration in the Liquid Phase

The iodometric method for residual ozone determination as described in Standard Methods (41) was used. The sample was collected in volumetric flasks containing 10.0 ml. of 10 per cent potassium iodide solution. 250 ml. samples of ozonised water were withdrawn from the sampling point through a Tygon tube, the end of which was held just above the surface of the liquid in the volumetric flask to order to minimise disturbance. This sampling procedure was used to minimise error due to entrainment of gas bubbles which may induce more absorption, hence resulting in an 'apparent' higher reading. The sampling procedure took 1.0 minute and any undissolved ozone passed to atmosphere. 10.0 ml. of 0.1 N sulphuric acid was added to the sample, and the titrations were carried out using 0.005 N sodium thiosulphate solution. Two samples were taken for each time interval. The samples were taken at various predetermined time intervals.

8.7.3 Determination of the Rate of Transfer of Ozone into Water and Its Distribution Coefficient

The rate of absorption of ozone is of great importance in assessing the performance of the rotating disc reactor. Because of the simultaneous decomposition of ozone in aqueous solution, it is also essential to know the fraction of dissolved ozone available for treatment of pollutants after decomposition. Hence we need to be able to predict the ozone concentration as a function of time in a contactor as well as the actual concentration of available dissolved ozone for a particular ozone feed concentration. The solubility of ozone in a dilute mixture of air or oxygen may be stated by referring to its 'Distribution Coefficient', 'D.C.', (or 'Solubility Ratio'), which may be defined for ozone as :

$$\text{D.C.} = \frac{\text{Conc. of ozone in water at a given temp. and pressure.}}{\text{Conc. of ozone in air at the same temp. and pressure.}}$$

Ideally the water used for mass transfer studies must not contain any contaminants which might catalyse the rate of ozone self-decomposition. Hence double distilled water was used for most of the runs. However, for those experiments whereby the system has to be operated continuously (Section 8.7.5) rather than batchwise, single distilled water was used because of the difficulties in collecting sufficiently large volumes of double distilled water. The water used for the mass transfer experiments was prepared as follows :

1. For batchwise runs, 20.0 litres of double distilled water was pre-ozonated in the glass isothermal batch reactor (reservoir) for 15 minutes to satisfy any ozone demand caused by contaminants. The water was then heated to almost boiling point to remove the dissolved ozone. It was then left to cool. A sample was then taken to test for dissolved ozone. This is to ensure the complete removal of dissolved ozone before each run.

2. The water used for the continuous runs (Section 8.7.5 :- determination of the mass transfer coefficient) was just ordinary distilled water without any pretreatment due to the extremely large volume required.

To determine the rate of transfer of ozone into water and its distribution coefficient, the system was operated in a semi-batch mode (i.e., continuously sparged gas to a constant volume of liquid). The glass reservoir was filled with 20.0 litres of pre-treated double distilled water. The test was performed at 20°C, and hence the reactor was kept overnight controlled at 20 °C. Before commencing the run, the temperatures at various points of the system were scanned (using thermocouples) by the data logger to ensure that the whole system has reached a steady state isothermal condition. The 20.0 litres of water was recycled continuously from the glass holding vessel (reservoir) via the rotating disc reactor and back to the reservoir. Samples were taken at the outlet of the reservoir. The samples were taken after 5, 10, 15, 30, 45, 60, 75, and 90 minutes intervals. This will enable us to determine the rate of absorption of ozone until it reaches its solubility limit for that particular ozone gas concentration. Hence saturation of the water was continued until it reaches a reliable maximum value, and although this was usually achieved in about 20 - 30 minutes, the procedure was continued for 90 minutes. At the end of one such run, the system was drained. The batch reactor (reservoir) was filled with another 20 litres of pre-treated water, and the determinations were repeated at the same temperature by using a different concentration of ozone. Hence, the rate of solution and the distribution coefficient at various levels

of feed ozone concentration were obtained at the temperature of 20 °C.

However in most practical injector system, the gas/water volume ratio normally used in water treatment is 1:2 or 1:3. Therefore, a further series of experiments were performed to evaluate the 'Fractional Distribution Coefficient' of ozone in water at 20 °C using a rotating disc reactor. The gas/liquid volume ratio employed was 1:2.59. This series of runs were performed with the system operating continuously and samples were collected at the outlet of the rotating disc reactor.

8.7.4   Effects of pH on the Decomposition of Ozone

Exact understanding of the decomposition mechanism of ozone in water is necessary as it will always mask mass transfer. Oxidation of certain substances by a direct reaction of molecular ozone are very selective and hence slow. However, reaction with certain of the ozone decomposition products often proceed at a faster rate than when reacting directly with the ozone molecule, (Sections 4.1, 4.2). Hence it is essential to study the variables affecting the decomposition of ozone in water in order to either enhance or reduce the ozone decomposition species as the situation may warrant.

The parameter investigated was the effect of pH on the decomposition of ozone. An attempt will then be made to apply these results to the treatment of effluents.

To determine the effects of pH on the rate of decomposition of ozone, the same batchwise procedure (Section 8.7.3) was employed except that the water used was buffered at different desired pH. The system was sampled regularly until equilibrium conditions were established. The pump and the ozone stream were then switched off and the unsteady state batch decomposition was determined by taking concentration-time measurements during decomposition. The pH investigated were pH 4.1, 7.1 ,8.2 and 9.2. The rapid decomposition of ozone at pH greater than 8.2 prevented accurate determination. The pH above 7.0 was maintained by buffering with sodium hydroxide and sodium bicarbonate, neither of which are oxidised by ozone. Sulphuric acid was used to maintain the acidic conditions because it is not oxidised by ozone. Analysis of liquid samples showed that the pH of the solution was not altered by ozone absorption.

8.7.5 Determination of the Mass Transfer Coefficient

To determine the mass transfer coefficient, the system was operated as a continuous reactor whereby distilled water was fed continuously from a few 40-litres holding tanks and the outlet liquid discharged into the drain. The runs were all carried out at 20 °C with a different inlet ozone gas concentration for each run. Analysis of ozone concentrations in both the gas and liquid streams were carried out only after steady state had been achieved. Samples were taken at the outlet of the rotating disc reactor. These data collected were then used to calculate the mass transfer coefficient, and the results were compared with the mass transfer coefficient calculated using Lim's (39) empirical correlation, (Section 6.1).

8.8 OZONATION OF EFFLUENTS

Samples of effluents were taken from a point after primary settlement and secondary settlement. Most of the samples used in this work were taken from a point after secondary settlement since the main objective of the research is to evaluate the prospect of using ozone as a tertiary treatment process. The samples were used as received after holding in a temperature controlled 20-litre glass reservoir for at least 12 hours. The same batchwise procedure (Section 8.7.3) was employed.

Sample characteristics such as pH, BOD, COD, TOC and M.P.N. (bacteria enumeration) were carried out as soon as the samples were received. Analysis of ozonated samples were done within two days of sampling. In between the intervals for different sanitary tests, the samples were held in a 4 °C refrigerator. The BOD and COD tests were performed according to the APHA methods. The modified Winkler method (Azide Modification) was used in this research for analysing BOD samples. A Beckman Model 915 Total Organic Carbon Analyser was used for determining the TOC. The Multiple Tube Method was used for bacteria enumeration (MPN). A Unicam SP800 Spectrophotometer was used for determining colour and turbidity. A full description of the chloroform extraction method used in determining phenol concentrations can be found in 'Standard Methods' (41).

8.8.1 Effects of pH on Ozonation

Earlier experiments on the effects of pH on the decomposition rate of ozone in water have led us to investigate the effects of pH on ozonation of effluents so as

to determine whether there would be an optimum pH for the treatment of this particular effluent.

8.9   OZONOLYSIS OF EFFLUENTS WITH AND WITHOUT SUSPENDED SOLIDS

To investigate whether ozone preferentially oxidises suspended solids, the secondary effluents were prepared by two different methods:

1. 20 litres of secondary effluent as received.

2. 20 litres of secondary effluent filtered through glass fibre filters (Standard Methods, 41) to remove the suspended particles.

The two samples were ozonated batchwise as described in Section 8.7.3 for 1.0 hour. Samples were withdrawn from the outlet of the glass CSTR reservoir at 10 minutes interval. The samples were tested for COD and TOC.

8.10   EFFECTS OF 'RESIDUAL OZONE' AND 'RESIDUAL AND GASEOUS OZONE' ON DISINFECTION

This experiment was carried out to investigate the effect of ozone on disinfection under different disolution methods, namely :

1. presence of ozone residual (i.e. ozone in the liquid) only.

2. simultaneous presence of ozone residual and ozone gas in the rotating disc reactor.

The rate of disinfection is a function of :

1. time of contact.

2. concentration of ozone.

3. number of organisms.

4. temperature of the liquid media.

In this study, the temperature was maintained at 20 ± 0.5 $^{\circ}C$. The time of contact and the number of organisms (M.P.N.) were the same for all the runs. Hence it is reasonable to assume that the rate of disinfection in this present work is only a function of ozone concentration.

These experiments were not performed batchwise as in Section 8.7.3 . Instead, a fixed volume of liquid was pumped from one holding tank, through the rotating disc reactor, and the outlet collected in another holding tank. The liquid was NOT recycled. Samples were taken for bacteria enumeration from the second holding-tank. A different ozone gas concentration was used for each run. To ensure positive results of % survival of bacteria, very low ozone doses were used for all the runs. (The objective of this set of experiment is just to investigate disinfection mechanism under different disolution methods).

1. Treatment with residual ozone only.
   9.0 litres of pretreated (Section 8.7.3) double-distilled water was pumped from a clean 20-litre holding-tank at a flowrate of 30 cc/s, through the rotating disc reactor into the 20-litre glass CSTR (previously used as a reservoir in the other runs), already containing 1 litre of diluted effluent with a known Total Coli count (M.P.N.). Two samples of the ozonated double-distilled water coming out of the rotating disc reactor were collected at the outlet before it enters the 20-litre glass batch reactor. This is to test for the dissolved ozone concentration in the ozonated water. The speed of the stirrer in the 20-litre glass CSTR was kept at 400 rpm. A simple pulse tracer experiment performed earlier indicated that a stirrer speed of 400 rpm would be sufficient to produce efficient mixing quite similar to that predicted by the theory of an ideal CSTR. For bacteria enumeration, two samples were taken AFTER 5.0 minutes of mixing in the CSTR from a sampling point at the outlet . Four runs were carried out, each with a different ozone feed concentration.

2. Simultaneous treatment with ozone residual and ozone gas.
   1 litre of the same diluted effluent with the same M.P.N. was added to 9.0 litres of pretreated double-distilled water in the 20-litre holding tank. The liquid was pumped at a flowrate of 33.0 cc/s through the rotating disc reactor and collected in the 20-litre glass CSTR. The stirrer of the CSTR was not switched on in this case. For bacteria enumeration, two samples were taken from the 20-litre CSTR IMMEDIATELY after all the liquid has been collected. It took 5.0 minutes to pump the 10.0 litres of liquid through the rotating disc reactor into the CSTR. Hence the 'contact time' in this experiment is essentially the same as in Case 1 (i.e., treatment with residual ozone only). The ozone concentration of the liquid was also determined. Four runs were carried out, each with a different ozone feed concentration. The different ozone feed concentrations chosen for each of these four runs were the same as the four ozone

concentrations used in Case 1 (i.e. treatment with ozone residual only).

8.11 OZONE/ULTRA-VIOLET OXIDATION OF EFFLUENTS, (OXYPHOTOLYSIS)

The same batchwise operation procedure (Section 8.7.3) was employed except that the effluents flowed from the glass reservoir, to the rotating disc reactor and then through the quartz photochemical reactor before flowing back into the reservoir to be recycled again. Samples were taken immediately after the quartz photochemical reactor. Initially, experiments were conducted with double distilled water so as to determine the equilibrium ozone concentration in water with and without ultra-violet radiation. This will enable us to determine how much of the ozone would be dissociated by the ultra-violet radiation. Experiments were then conducted using secondary effluents to determine the effects of ozone/U.V. oxidation on treatment rate. The runs were conducted only after allowing several minutes for the U.V. lamp to attain the rated power levels.

Two types of mercury lamp (low and medium pressure) are normally used for photochemical reactions. Low pressure lamps emit over 90 % of their radiation at 254 nm. Medium pressure lamps have much more intense arcs and radiate predominantly 365 - 366 nm radiation with smaller amounts in the ultra-violet region at 265, 297, 303, 313 and 334 nm as well as significant amounts in the visible region at 404 - 408, 436, 546 and 577 - 579 nm. The absolute output in watts at different wavelengths for each 100 watts of loading on the tube for a typical medium pressure U.V. arc-tube in quartz operating at above 800 mm internal pressure is shown in Table 3. The ultra-violet source used in this work was a medium pressure lamp (Model 3040 - Applied Photophysics Ltd.). The reason for using a medium pressure lamp was because of its availability in the Department and also because of the fact that all previous work done recently in the U.S. by other investigators on ozone/U.V. oxidation were performed with low pressure lamps. Presumably low pressure lamps may be more effective for ozone photochemical reactions since it is more effective in the dissociation of ozone. However much more work needs to be done to determine the effects of wavelength on ozone photochemistry.

The characteristics of the lamp used in this work are :

Nominal wattage	Overall length (mm)	Diameter (mm)	Light output *
400	255	25	$> 5 \times 10^{19}$

* :- Photon/s measured by ferrioxalate actinometry.

Calculation of the effective energy available :
Planck's constant, $h = 6.634 \times 10^{-34}$ J.sec.
Velocity of light, $c = 2.999 \times 10^{8}$ m/sec.
Predominant wavelength, $w = 365$ nm
Frequency of light $v = c/w$
                          $= 8.214 \times 10^{14}$ cycles/sec.
Energy $E = hv$
                          $= 0.545 \times 10^{-18}$ J/photon.
Light output (Model 3040) $= 5 \times 10^{19}$ photon/sec.
Therefore, ENERGY/SEC. $= 27.25$ Watts.

Table 3 : Absolute output in watts at different wavelengths, for each 100 Watts of loading on the tube, for a typical medium pressure U.V. arc-tube in quartz operating at about 800 mm, internal pressure.

Wavelengths in nm		Intensity in watts
235	-	0.12
238	-	0.23
240	-	0.21
246	-	0.09
248	-	0.53
254	-	0.68
258	-	0.08
260	-	0.11
264	-	0.14
265	-	0.98
270	-	0.23
275	-	0.17
280	-	0.55
289	-	0.26
292	-	0.11
297	-	0.74
302	-	1.42
313	-	2.72
334	-	0.37
366	-	4.30
391	-	0.06
405	-	1.14
406	-	0.24
436	-	2.10
492	-	0.06
546	-	2.76
577/9	-	3.42
691	-	0.08
1014	-	1.18

9   RESULTS AND DISCUSSION

This chapter will review the results obtained in the
present study and compare the results, wherever possible,
with pertinent published data. The data on mass transfer of
ozone will be discussed in the light of available information
regarding the value of the 'distribution coefficient',
decomposition rate constant, and the value of the mass
transfer coefficient of ozone in water using a rotating disc
reactor. Detailed discussion will include the effects of
ozonation on the sanitary characteristics of the
multicomponent refractory bearing effluents and a discussion
will also be presented on the effects of ozone/U.V.
oxidation. A conceptual model for the oxidation of effluents
using residual ozone (dissolved ozone) alone and using
residual ozone with gaseous ozone (at the gas/liquid
interface) will be postulated. Detailed discussion will
include the efficiency of the rotating disc reactor as a
contacting device for ozonation processes.

Results of all the experiments of this research work will
be presented in either tabular or graphical form, or both.
In each case, the data represents the average of at least two
separate runs on each sample.

9.1   MASS TRANSFER STUDIES

9.1.1   Determination of the Rate of Transfer of Ozone into the
                 Water and its Distribution Coefficient

The results on the rate of transfer of ozone into the
water on the rotating disc is shown in Fig.(6). The data
showed that the ozone concentration in the liquid increased
exponentially to the solubility limit. Since all the runs
were performed under the same hydrodynamic conditions, the
initial slopes of the concentration build-up curves would be
the same, as shown in the figure. Ozone dissolves rapidly in
the water. The saturation point for a particular input ozone
gas concentration could be reached within 20 - 25 minutes.
Hence, in terms of attaining maximum solubility, it is only
necessary to recycle 20.0 litres of liquid at 30.0 cc/s
twice.

Different ozone gas concentration gave a different
equilibrium ozone liquid concentration. The dissolved ozone
concentration is proportional to the concentration of ozone
applied. This indicates that Henry's Law is obeyed. The

'distribution coefficient' of the gas is defined as the ratio of the concentration of ozone in the water to the concentration of ozone in the gas. This distribution coefficient is obtained from the maximum reliable value (Fig. 5) of the dissolved ozone concentration at each applied ozone concentration. Hence the maximum distribution coefficient (batch mode operation) of ozone in water at 20 °C for different concentrations of applied ozone is found to be 0.24.

When a gas/water volume ratio of 1:2.50 was used, the 'fractional distribution coefficient' was found to be 0.21. Hence, the approach to maximum distribution coefficient (calculation based on the maximum distribution coefficient at 20°C of 0.24) is about 85.8 %.

9.1.2   Effects of pH on the Decomposition of Ozone

The overall simplified decomposition mechanism can be expressed as :

$$2\ O_3 \longrightarrow 3\ O_2$$
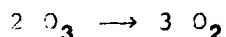
and the rate of decomposition of ozone can be expressed as :

$$-r_{O_3} = -d(O_3)/dt = k(O_3)^n$$

where k = reaction rate constant.
n = order of the reaction.

Concentration-time data are plotted for all the runs, Fig.(7). They follow a similar characteristic. There is an initial rapid decrease in the dissolved ozone concentration, followed by a decrease which could be approximated by a first order rate. Hence, assuming that the kinetics of ozone decomposition in aqueous solution is 1st. order with respect to the ozone concentration, a plot of the log of the dissolved ozone concentration against time should yield a straight line. A linear regression program using the method of least squares can be used to correlate the data to determine the reaction rate constants.

The plot of the log of dissolved ozone concentration against time yielded a straight line for all the three pH investigated, Fig.(8). This indicates that a first order rate can satisfactorily describe the decomposition over the pH range from 4.1 to 8.2. With solutions of pH greater than 8.2, the decomposition of the ozone cannot be monitored accurately. However it is still possible to measure accurately the maximum attainable dissolved ozone concentration.
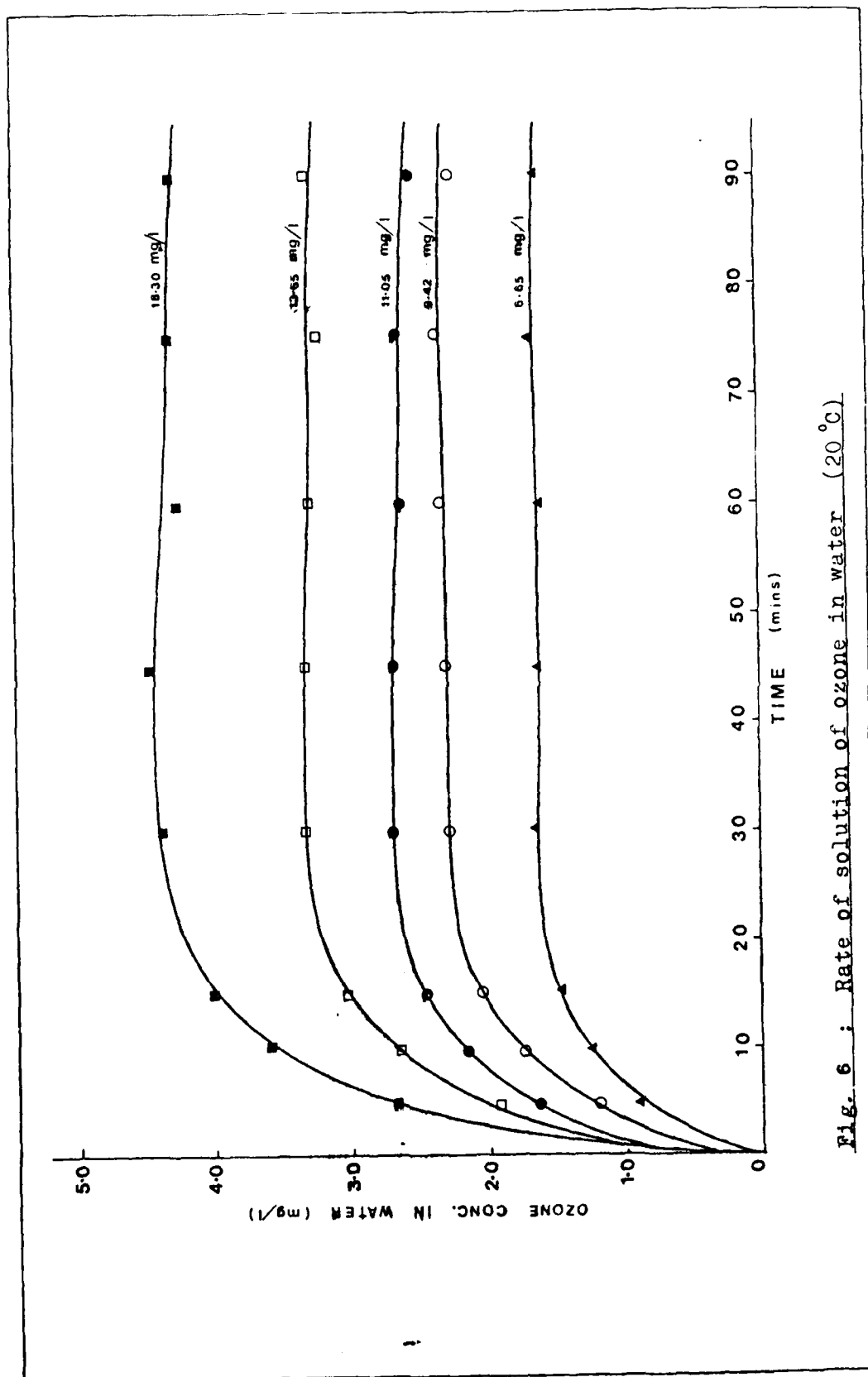
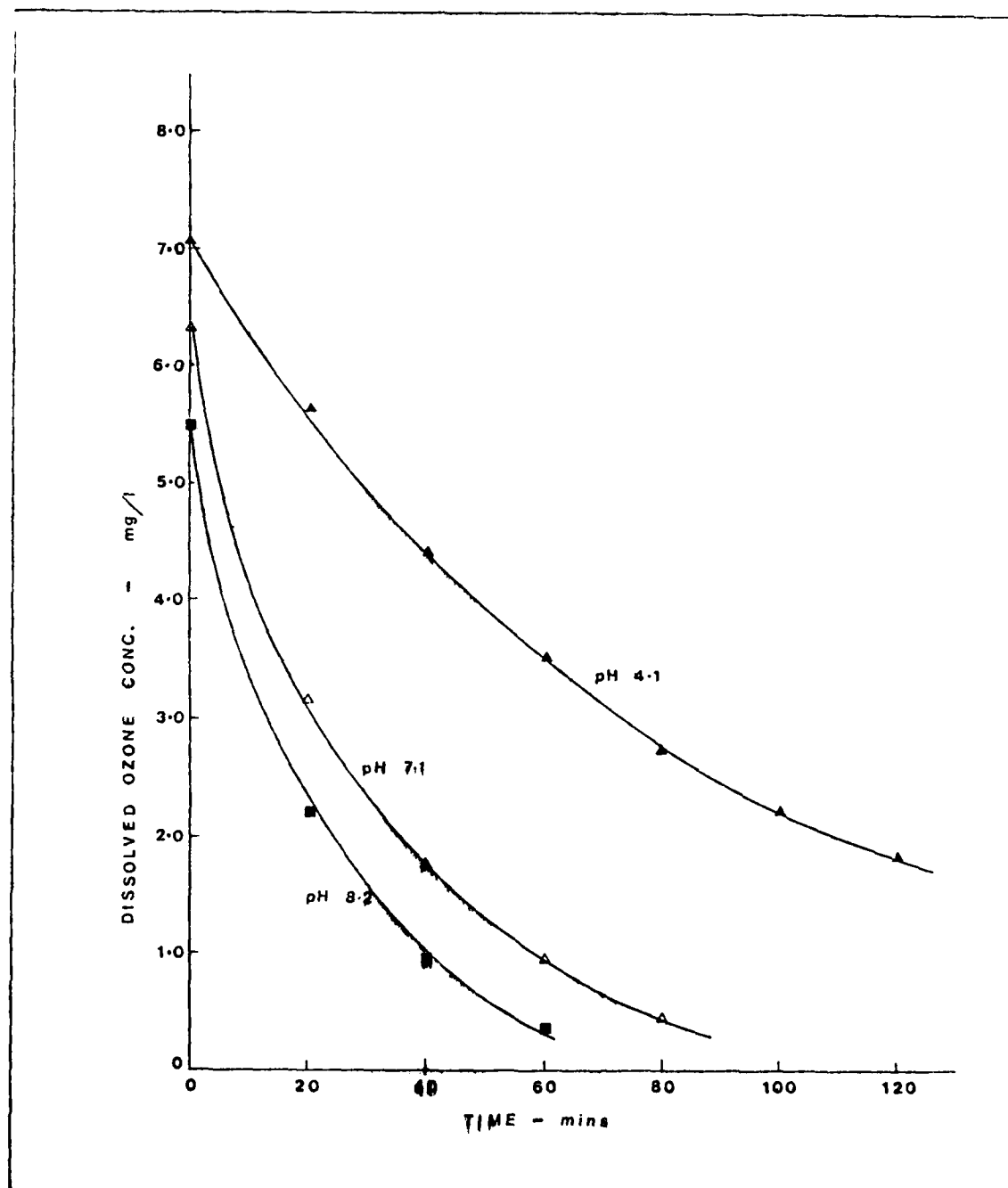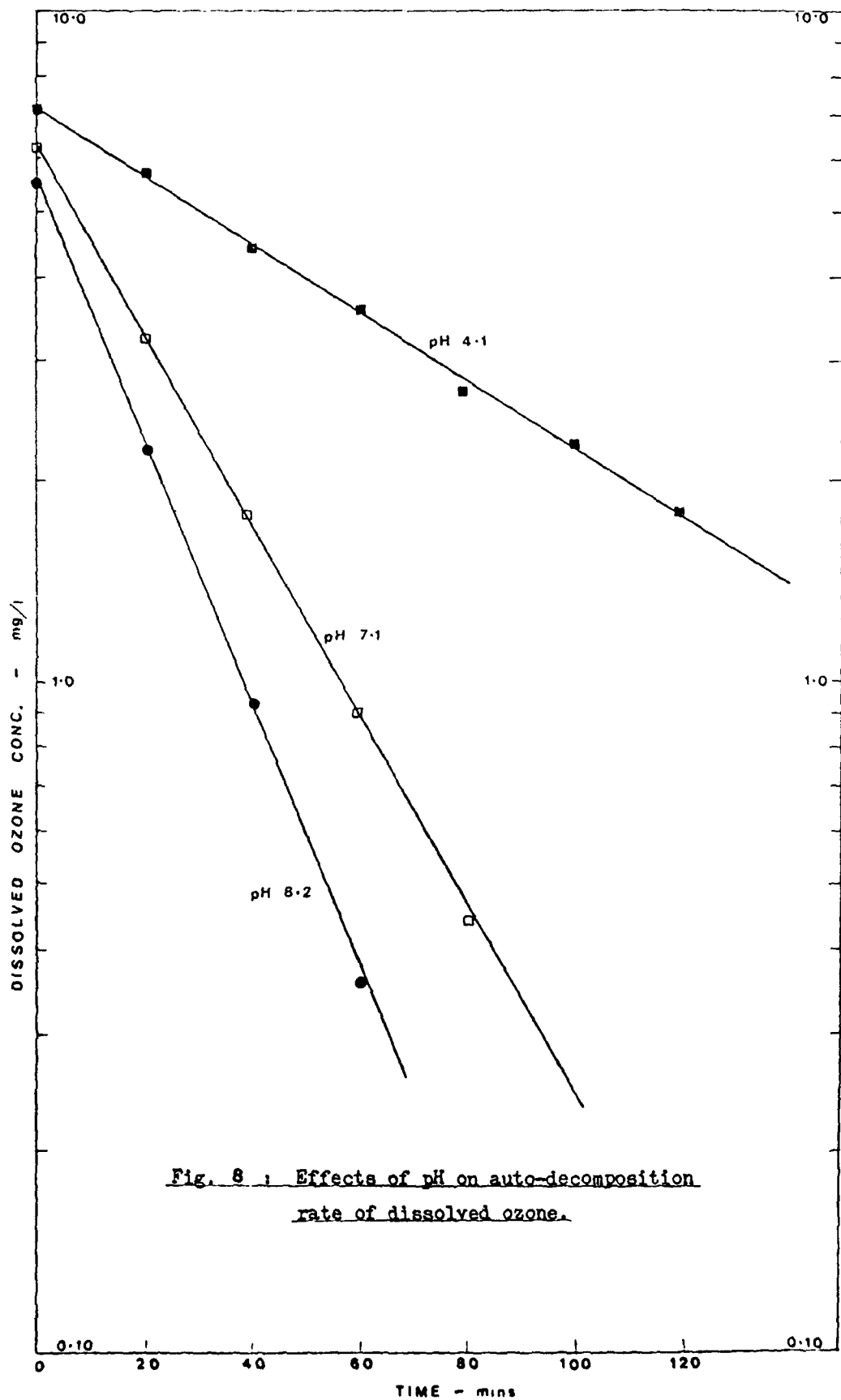Fig. 6 : Rate of solution of ozone in water (20 °C)

Fig. 7 : Ozone concentration - Time Curves.

Fig. 8 : Effects of pH on auto-decomposition rate of dissolved ozone.

Other conclusions can be drawn from this study as well. Fig.(9) shows that a decrease in pH results in a higher steady state dissolved ozone concentration. An increase in pH results in a lower level of steady state dissolved ozone concentration attainable. The reaction rate constant increases with pH value, Fig.(10). As can be seen from the 'initial' slopes of the concentration-time curves (Fig. 7), there is an increase in the rate of ozone decomposition with pH values. This will result in a shorter half-life of ozone.

9.1.3 Determination of Mass Transfer Coefficient

Two approaches will be taken in order to evaluate the mass transfer coefficient for ozone into water :

1. Calculate the coefficient using published empirical correlations, Lim(39) and Porter,J.E.,(42). The results will be acceptable if ozone behaved similar to the gases used in developing the correlations (i.e. oxygen).

2. Measure the mass transfer coefficients experimentally :- our present rotating disc reactor is sufficiently similar to that used by the above investigators. Great care was taken to ensure that our mass transfer runs were carried out with minimum chemical reaction. The data obtained was then used to evaluate the mass transfer coefficients and the results compared with that calculated with the proposed empirical correlation.

The experimental mass transfer coefficient is found to be 4.1 x 10^{-4} m/s and the value of the mass transfer coefficient calculated using similar physical operating conditions from this equation, (Section 6.1) :

$$Sh = 4.76 \times 10^{-8} \, Re^{0.68} \, Ta^{0.37} \, R^{*-0.53} \qquad \ldots \ldots (6.4)$$

is 4.7 x 10^{-4} m/s. Details of the calculations are shown in Appendix B. According to the most recent research results, the coefficient for ozone is of the order of 2 x 10^{-4} m/s, (Masschelein,43). Unfortunately, not much work has been done in this field.
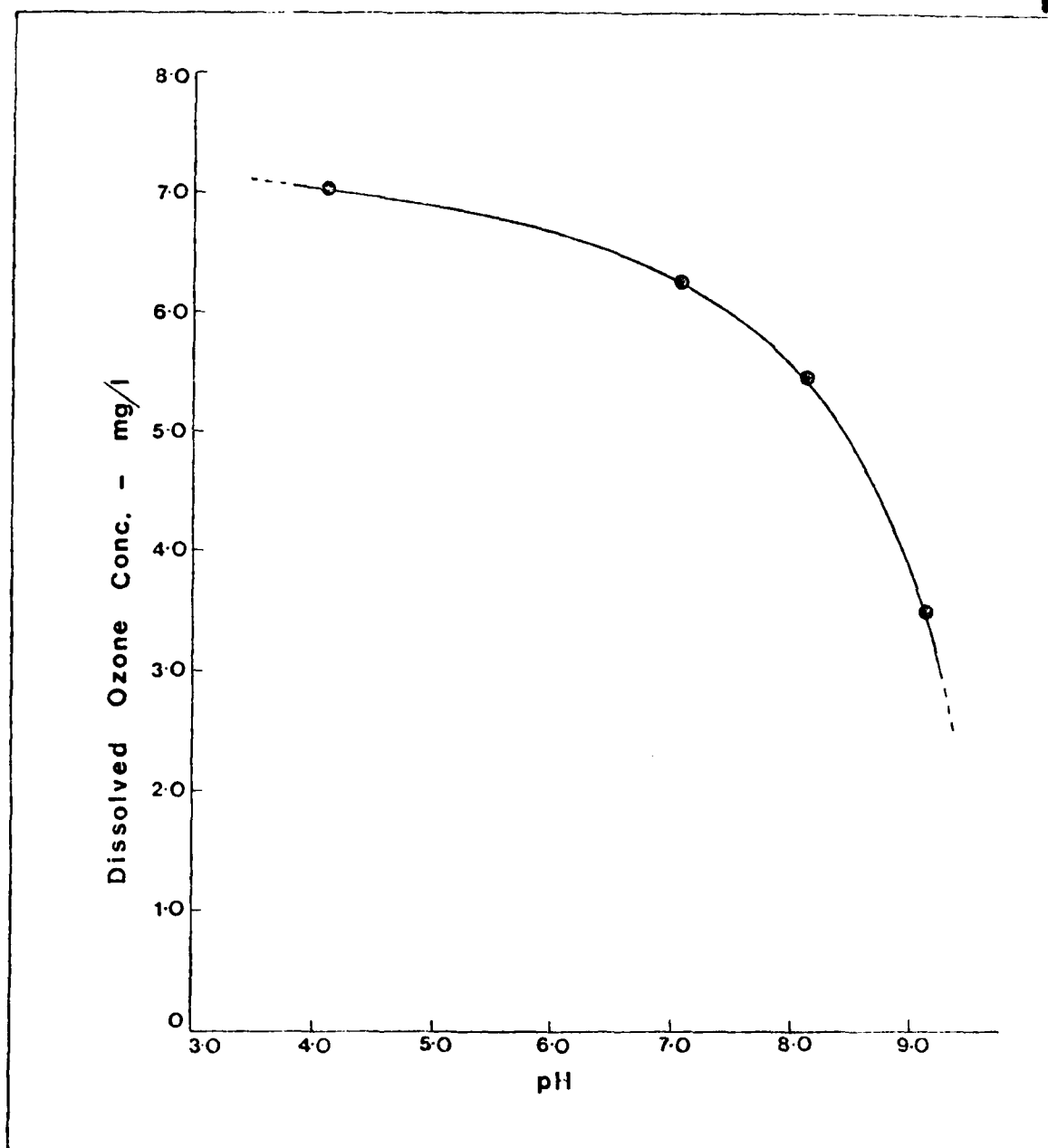
Fig. 9 : Effects of pH on the steady-state
dissolved ozone concentration.

9.2   OZONATION OF EFFLUENTS

### 9.2.1   Effects of Ozonation on Primary and Secondary Multicomponent Effluents

The TOC of primary samples were much higher than that of the secondary samples, and as shown in Fig.(11), the ozone utilisation were more efficient BUT the quality of the treated effluent were poorer. A comparison of the slopes of each curve suggests that the ozone efficiency for TOC reduction increases with increasing TOC levels in the sample. This shows that the more readily oxidisable organic compounds in the effluent consume ozone more readily. Hence, ozonation is not a suitable method for the treatment of primary effluent because of the enormous quantity of ozone required for the treatment. It is more cost effective for the more readily oxidisable compounds to be initially removed by some other cheaper methods of treatment.

However in the case of tertiary treatment, we are dealing with the treatment of an effluent whose sanitary qualities can no longer be improved by conventional methods. Even so, as the quality of the treated effluent improved, the efficiency dropped because more ozone was passing out of the liquid phase unreacted. But, as will be discussed later, tertiary treatment of effluent can be made to be extremely efficient. The fact that a TOC reduction was achieved in tertiary treatment demonstrates the oxidising capabilities of ozone in the destruction of organics refractory to biological treatment. A reduction in TOC only occurs when there is a complete destruction of the organic residue (remaining after conventional biological treatment) to carbon dioxide.

9.2.2   Results achieved in Tertiary Treatment by Ozonation

The following water quality characteristics were observed after ozonation of the secondary multicomponent effluents. Most of them will be discussed in greater details in the following sections.

1.   Reduction in BOD, COD and TOC.

2.   Reduction of colour and odour.

3.   Decrease in turbidity.

4.   Suspended solids reduction.

Fig. 10 : Effects of pH on Specific Rate Constants.
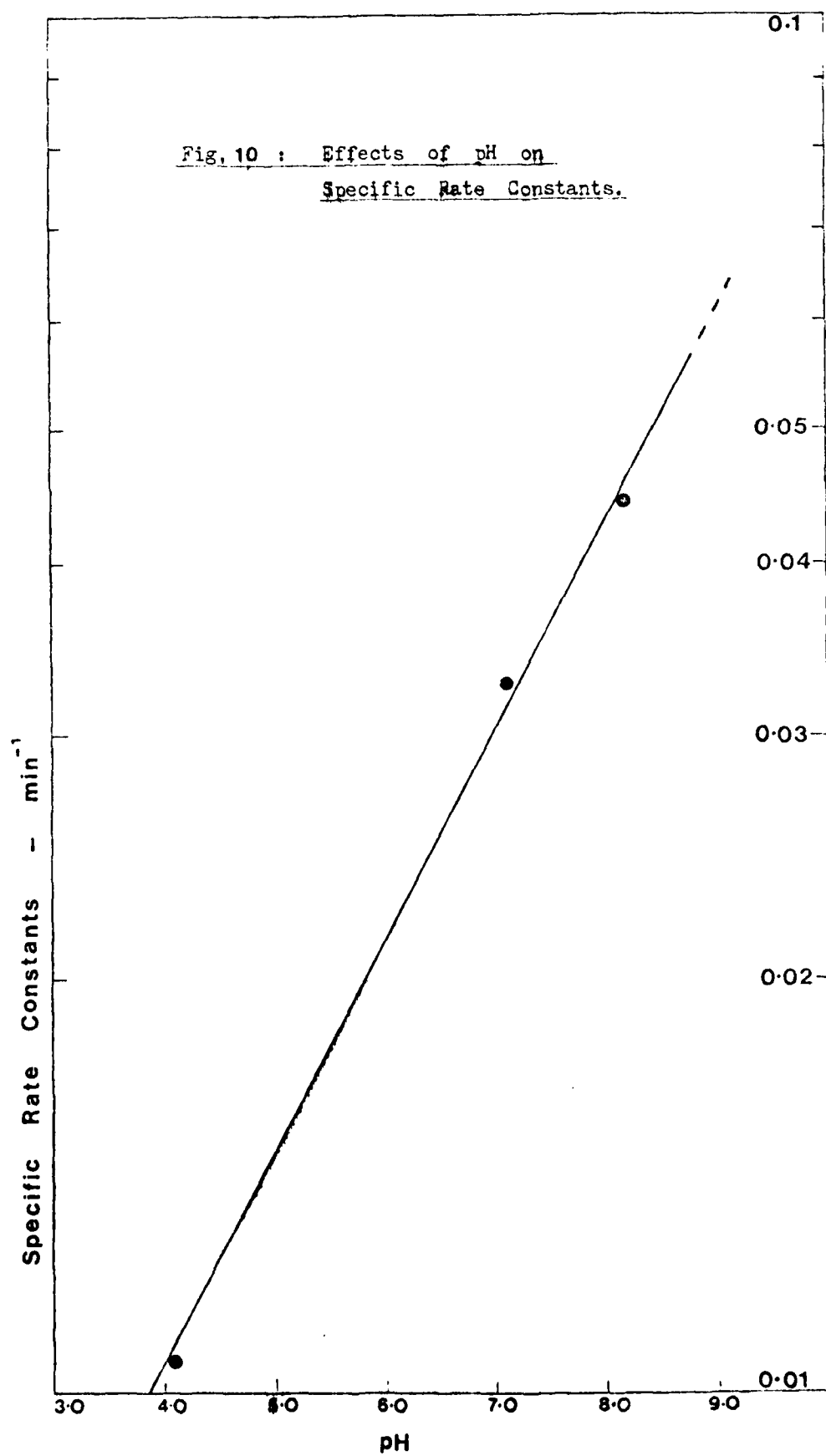
5. Disinfection.

6. Improves the biodegradability of refractory substances.

7. The pH of the samples does not seem to fluctuate much during ozonation.

8. Increase in dissolved oxygen content - up to a maximum of about 40 mg/l (with oxygen feed to the ozone generator).

9.2.3 Reduction of BOD, COD and TOC

Using two broad ranges of effluents with BOD of (30 - 50)mg/l and (50 - 80)mg/l, with each point representing the average of two measurements, it was observed that there was a decrease in the BOD after ozonation, Fig.(12). However, when a highly coloured effluent was used, the BOD actually increases by about 14% during the initial part of the run. The most probable explanation for this phenomenon is the fact that the ozone oxidises some of the nonbiodegradable material to a biodegradable form which therefore exerts additional oxygen demand.

The COD removal curve shows that the reaction rate is extremely rapid initially but decreases after about 60 % of the COD is removed, Fig.(13). The shape of the 'TOC versus Time' curve is almost identical to that of the COD removal curve, except that the initial reaction is much slower. This is due to the fact that the decrease in TOC is NOT an indication of 'partial oxidation', but of TOTAL oxidation. Therefore, during the first few minutes of ozonation, partial oxidation products are formed, resulting in a rapid decline of COD and a relatively slower decrease in TOC.

Hence, while the reduction of COD indicates a response to ozonation, no clevage of the organic molecules is necessary for a COD reduction. On the other hand, a reduction of TOC occurs only on destruction of the organic compounds to carbon dioxide and water. The TOC gives the absolute content of organic carbon. The COD/TOC ratio can be used as an indication to evaluate the extent to which organics are oxidised. It gives an indirect measure of the oxidation state of organic carbon in the wastewater.
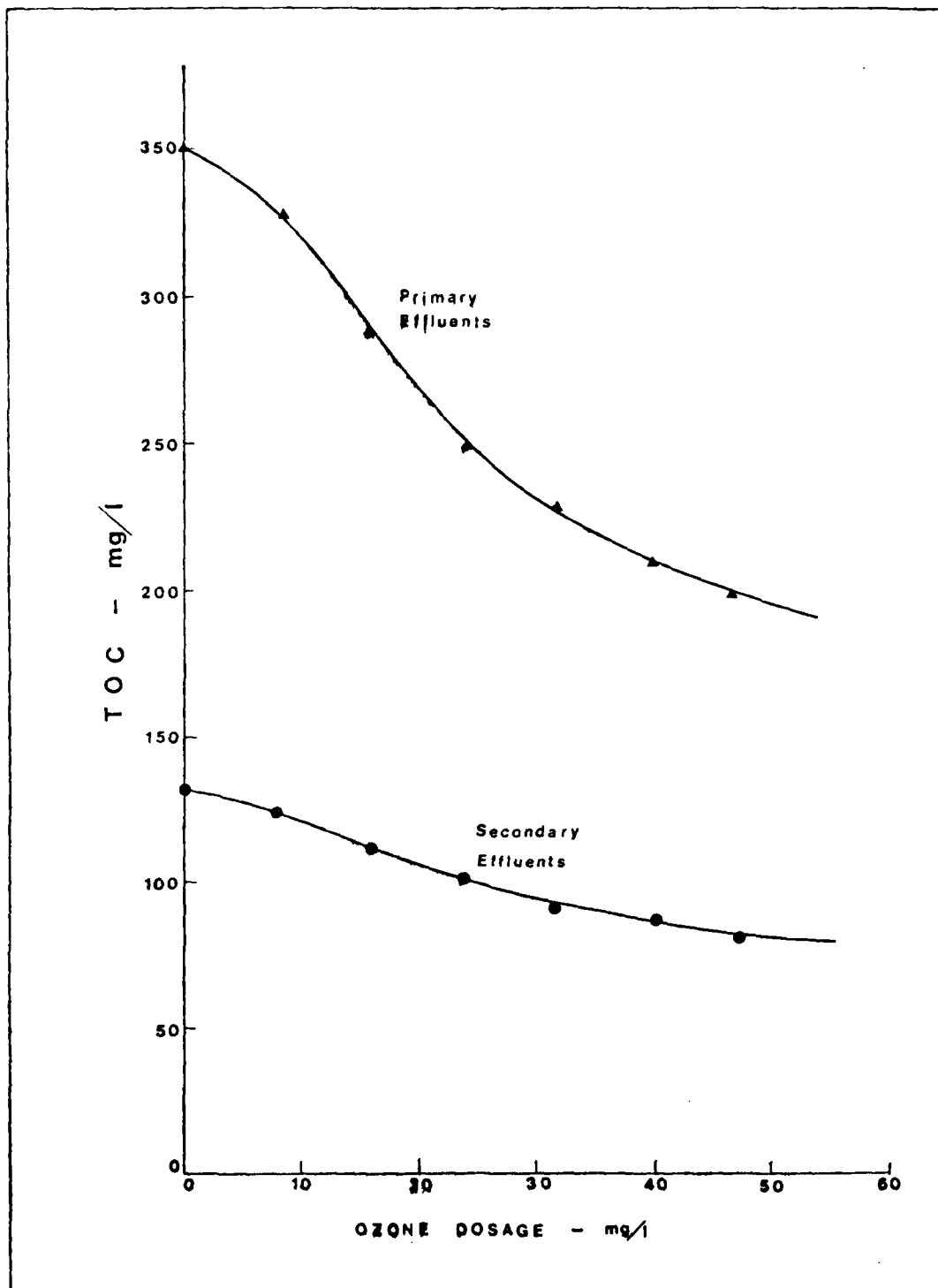
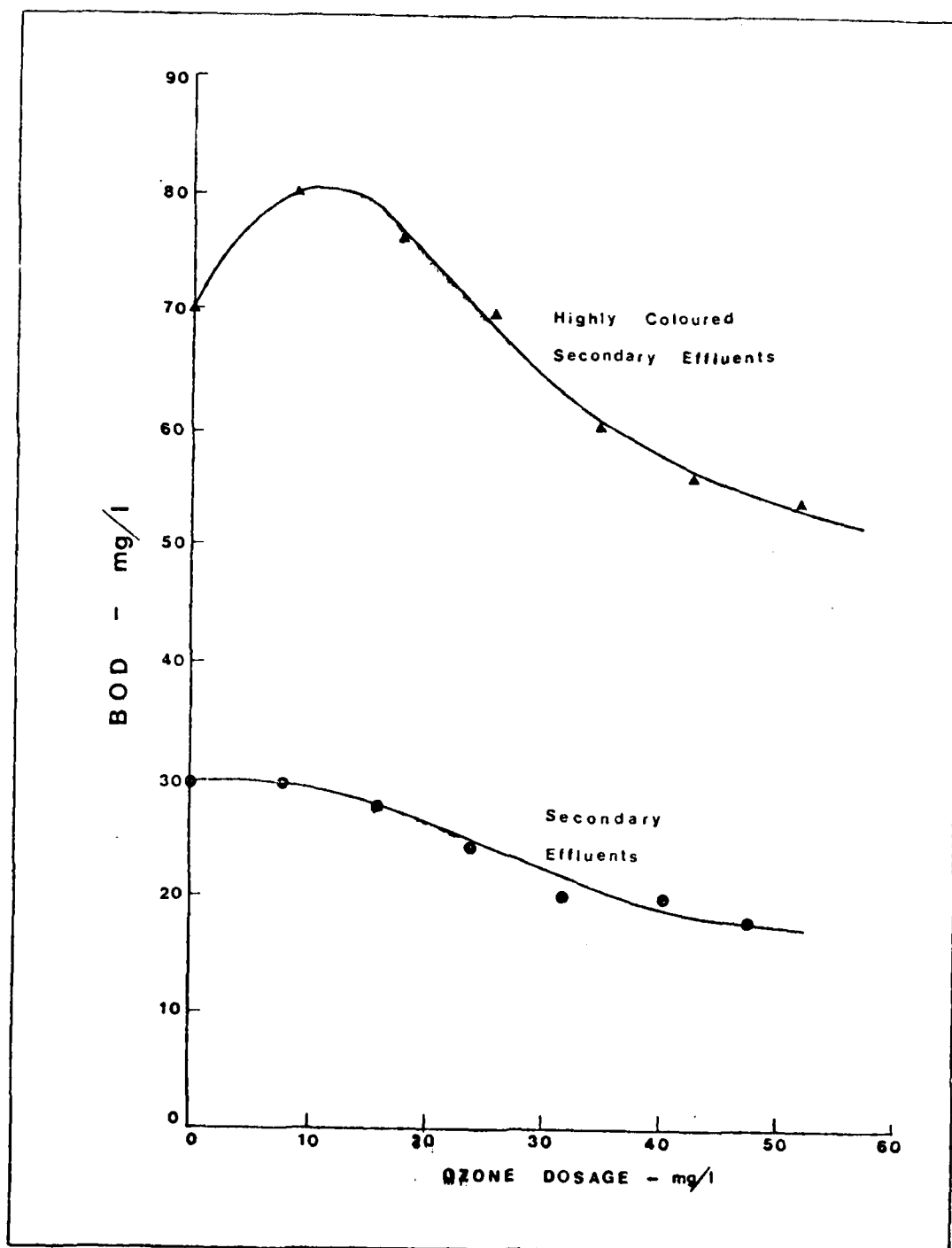Fig. 11 : T O C Reduction in Primary
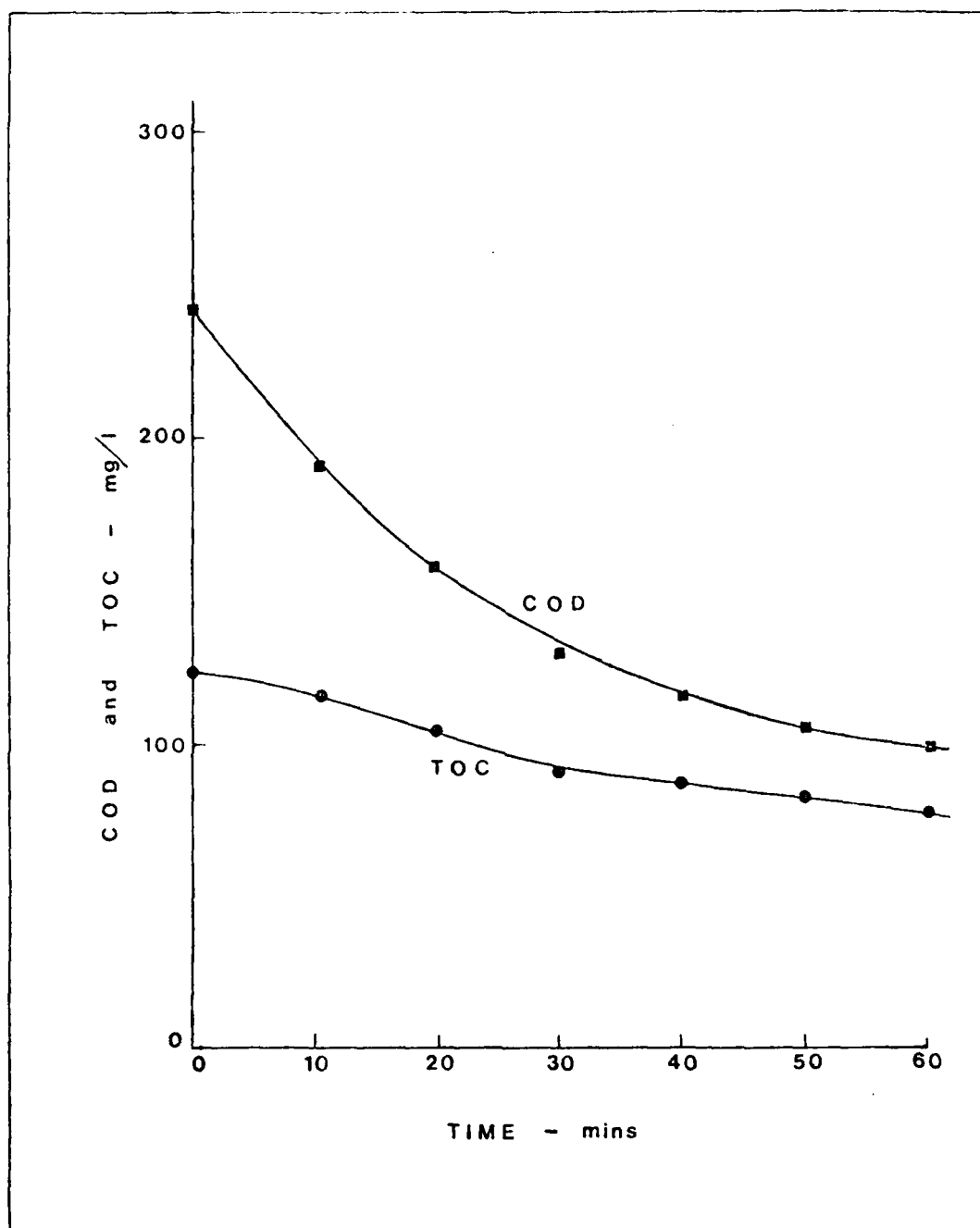and Secondary Effluents.

Fig. 12 : Effects of ozone on B O D.

Fig. 13 : Effects of ozone on C O D and T O C.

9.2.4 The Efficiency of the Oxidation Process

The COD/TOC ratios are a convenient means of monitoring the efficiency of an oxidation process. They may be interpreted as grams of oxygen required for oxidation per gram of carbon. It gives an indication of the oxidation state of the carbon. The COD/TOC ratio is proportional to the inverse of the oxidation state.

Table (4) shows the 'initial' and 'ozonised' COD/TOC ratios of four of the samples of different quality. Only four examples are listed in the table because these four ratios highlight the variability in sanitary quality of the samples (as indicated by the distinct differences in the 'initial' COD/TOC ratios) collected from the same source at different times. The higher values of some of the ratio shown in the table indicates that those particular samples were less oxidised. This variation shows that the nature of the organics fluctuates between samples.

The table shows that the COD/TOC ratios for the ozonised samples are less than the corresponding ratios for the original samples. This indicates that all of the remaining organics are now more oxidised than the original samples. Fig.(14) shows a qualitative evaluation of the oxidation pathway being followed in the TOC removal reaction by plotting the COD/TOC ratios over the entire treatment period of one of the samples (best representative of all the samples). The figure shows that the ratio decreases from 2.45 to about 1.70 after ozonation.

9.2.5 The Reaction Rate of Treatment

Fig.(13) shows a typical COD reduction curve in which the initial reaction is rapid, but the oxidation rate decreases as the reaction proceeds. In Fig.(15) the same data is used to plot 'Log COD versus Time'. It can now be seen clearly that the initial reaction is very fast, but after about 60 % reduction, the nearly zero slope suggests that the reaction rate decreases drastically. One reason for this could be the presence of a refractory class of compounds in the effluents which cannot be oxidised by ozone. Alternatively, only a very slow oxidation occurs which cannot be deduced from the change in slope of the graph. Hence, a separate experiment was conducted whereby the effluents was recycled through the rotating disc reactor for 3 hours to obtain the 'end-point' of the COD. The same data can now be analysed in another manner. To interpret these results, a graph of 'Log COD' (normalised to feed COD) against 'Log Reaction Time' is

Table **4** : C.O.D./T.O.C. Ratios of
Secondary Effluents before and after
ozonation*

Initial C.O.D./T.O.C. Ratio	Ozonised C.O.D./T.O.C. Ratio
1.85	1.30
1.92	1.28
2.45	1.71
3.37	2.25

* The above examples were chosen to show the
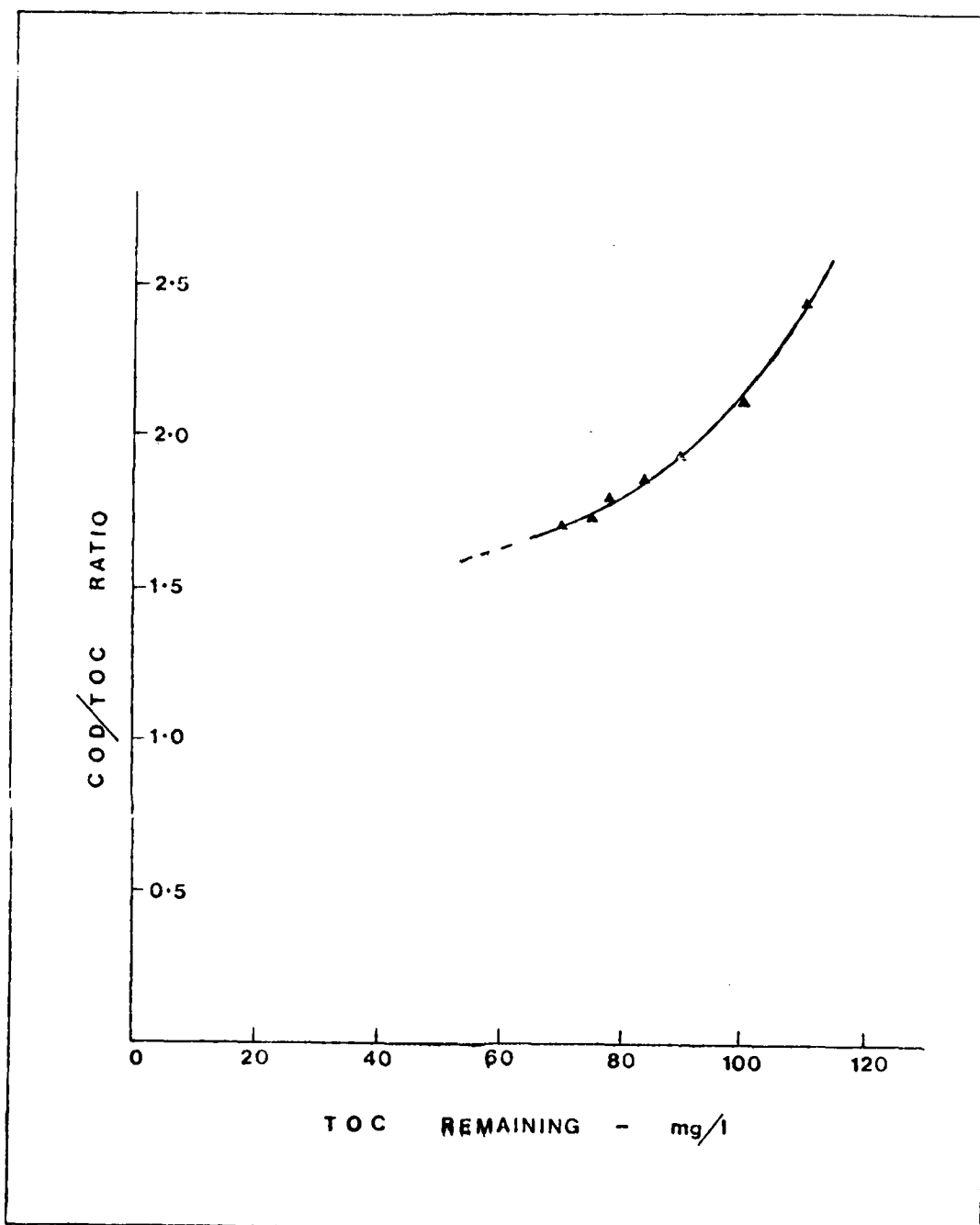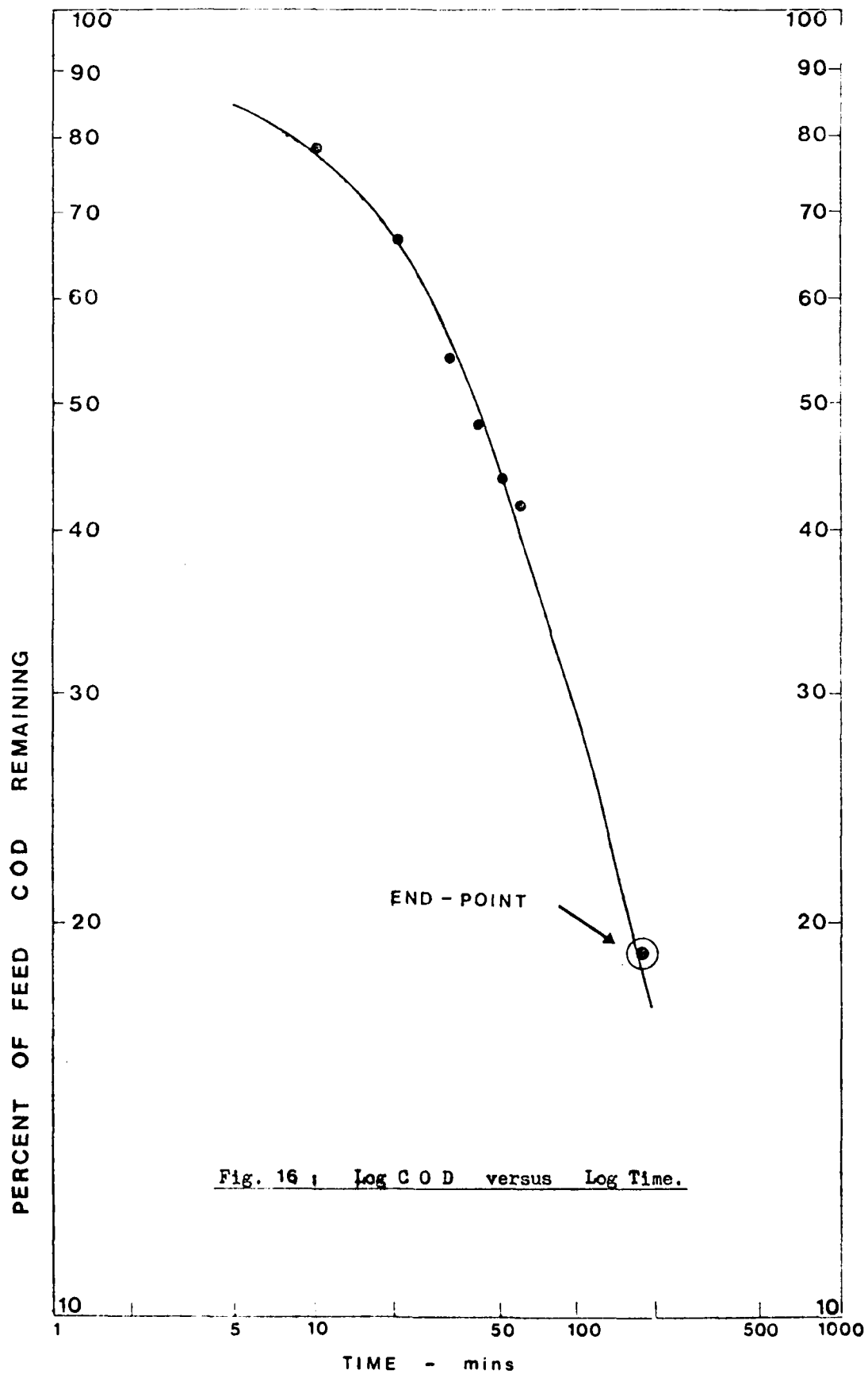variability of the sample characteristics

Fig. 15 :   Log C O D   versus   Time.
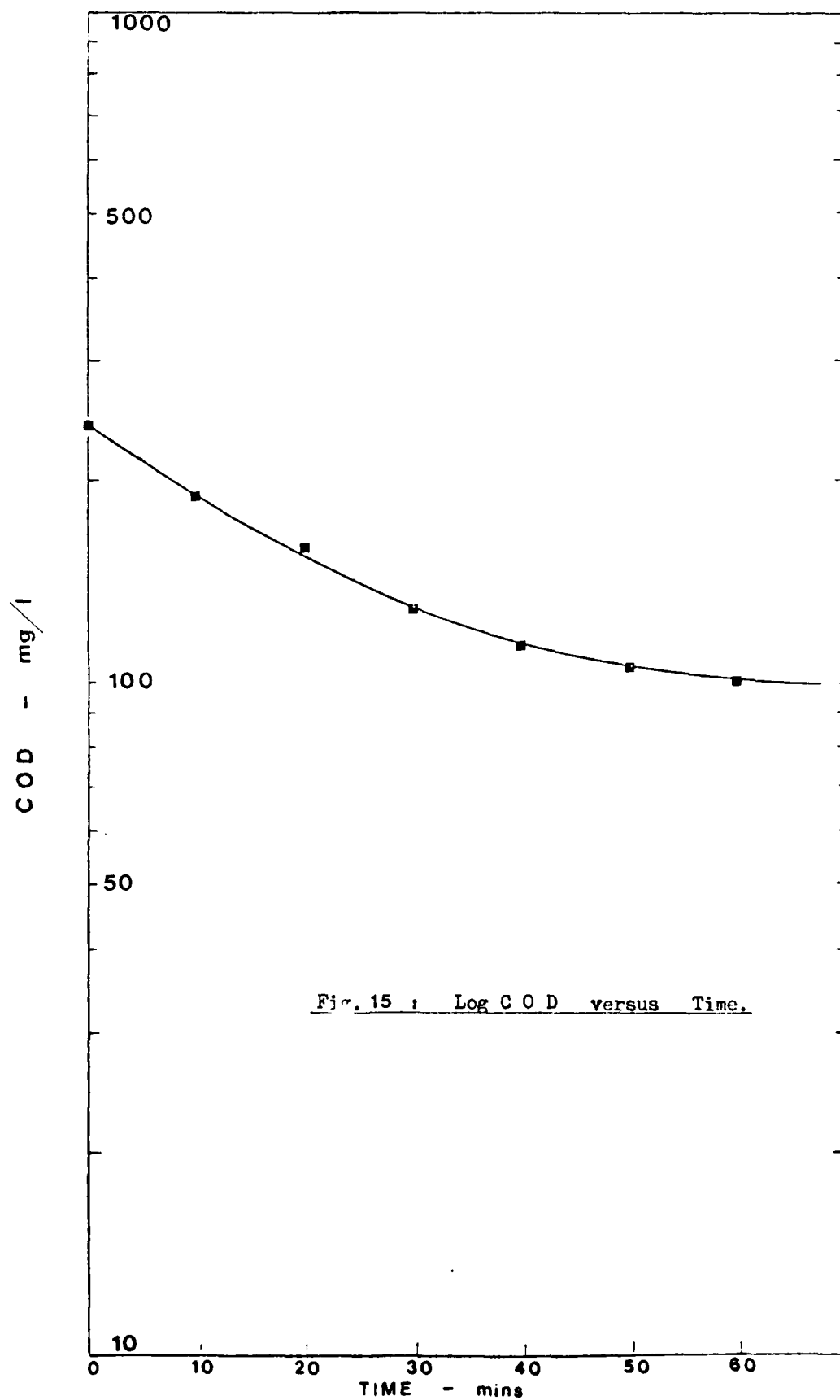
Fig. 14 :   Organic   carbon   oxidation   pathway.

END – POINT

Fig. 16 :   Log C O D   versus   Log Time.

PERCENT OF FEED C O D REMAINING

TIME – mins

plotted, Fig.(16).This time, the 'end-point' obtained from the extended ozonation test is included. The convex shape of this graph provided evidence that essentially all of the COD constituents of the effluents are slowly oxidisable by ozone eventually. However, the treatment time required is so great that after 70 % to 80 % reduction, further treatment is not justifiable economically .

9.2.6   Ozonation and Biodegradation

As stated in Section 9.2.3, when a highly coloured effluent was used, the BOD actually increased before decreasing after additional amount of ozone has been absorbed. In these runs, changes in BOD were measured along with colour removal. A plot of the 'Percent Change in BOD' versus 'Colour Conversion' is shown in Fig.(17). It shows that initially ozone causes the formation of biodegradable species ALONG with colour removal. The curve also shows that these biodegradable species are eventually destroyed as colour removal increases. The removal of colour does not necessarily mean a complete destruction of the colour-causing compounds (Section 9.2.8 and 9.2.9).

Ozone introduces oxygen functional groups into the refractory compounds and these new oxygen functional groups provide bacteria a site where metabolism can occur. Hence there is an increase in the oxygen demand (BOD). Further application of ozone will eventually oxidise these compounds, resulting in the decrease in BOD.

As discharge standards are raised, it is suggested that more work should be carried out to investigate whether the partial oxidation of biorefractory compounds to a biodegradable form followed by the conventional biotreatment is economically feasible.

9.2.7   Effects of pH on Ozonation

Fig.(18) shows that up to a certain value of pH, the TOC removal rate increases with pH. This is most probably due to the mechanism of ozone decomposition resulting in free radicals. The treatment rate obtained for pH 8.2 and pH 9.2 were almost identical, and at pH 11.0 it falls dramatically. The enormous depletion of dissolved ozone due to higher decomposition rates at pH greater than 9.2 is undesirable in the treatment. Hence a pH of 8.2 is considered optimum for the treatment of this particular effluent. Although the errors in measurement of dissolved ozone in effluents are
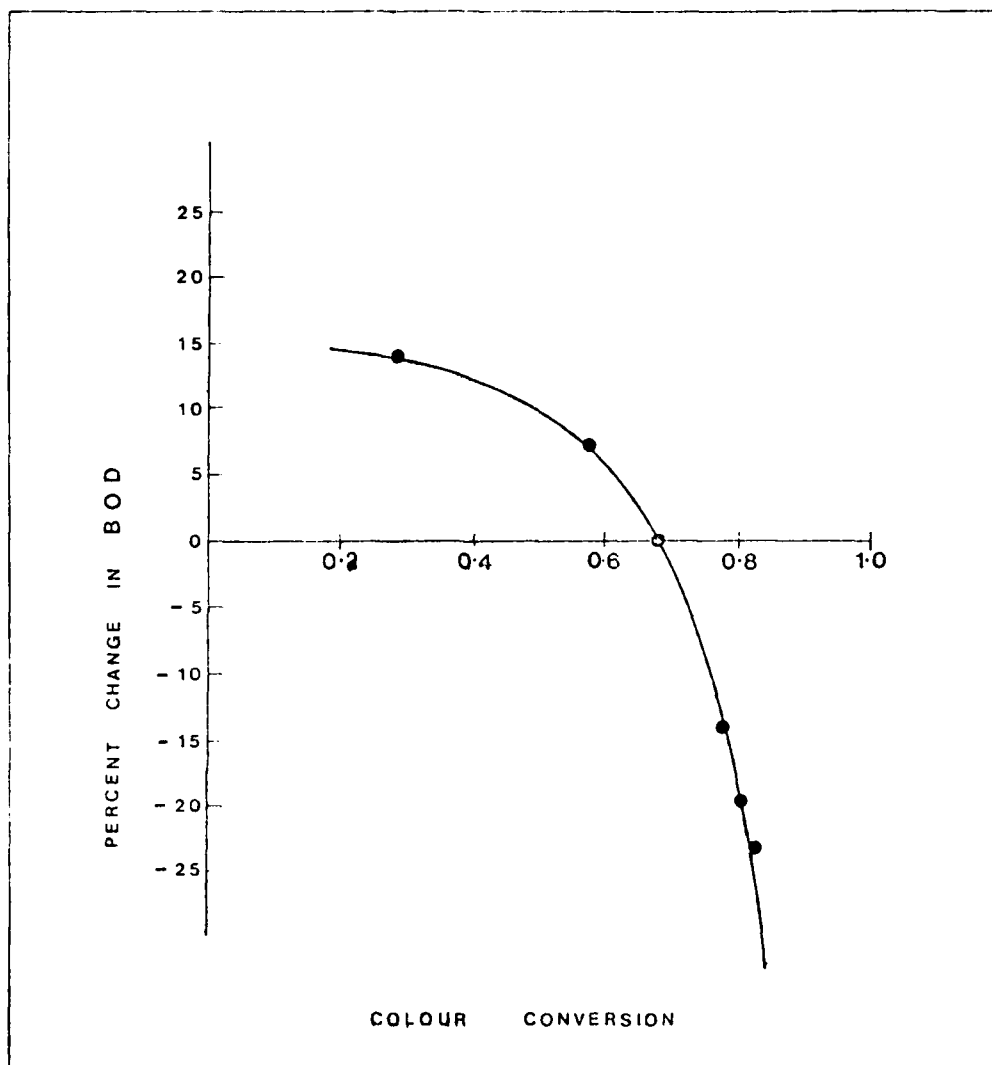
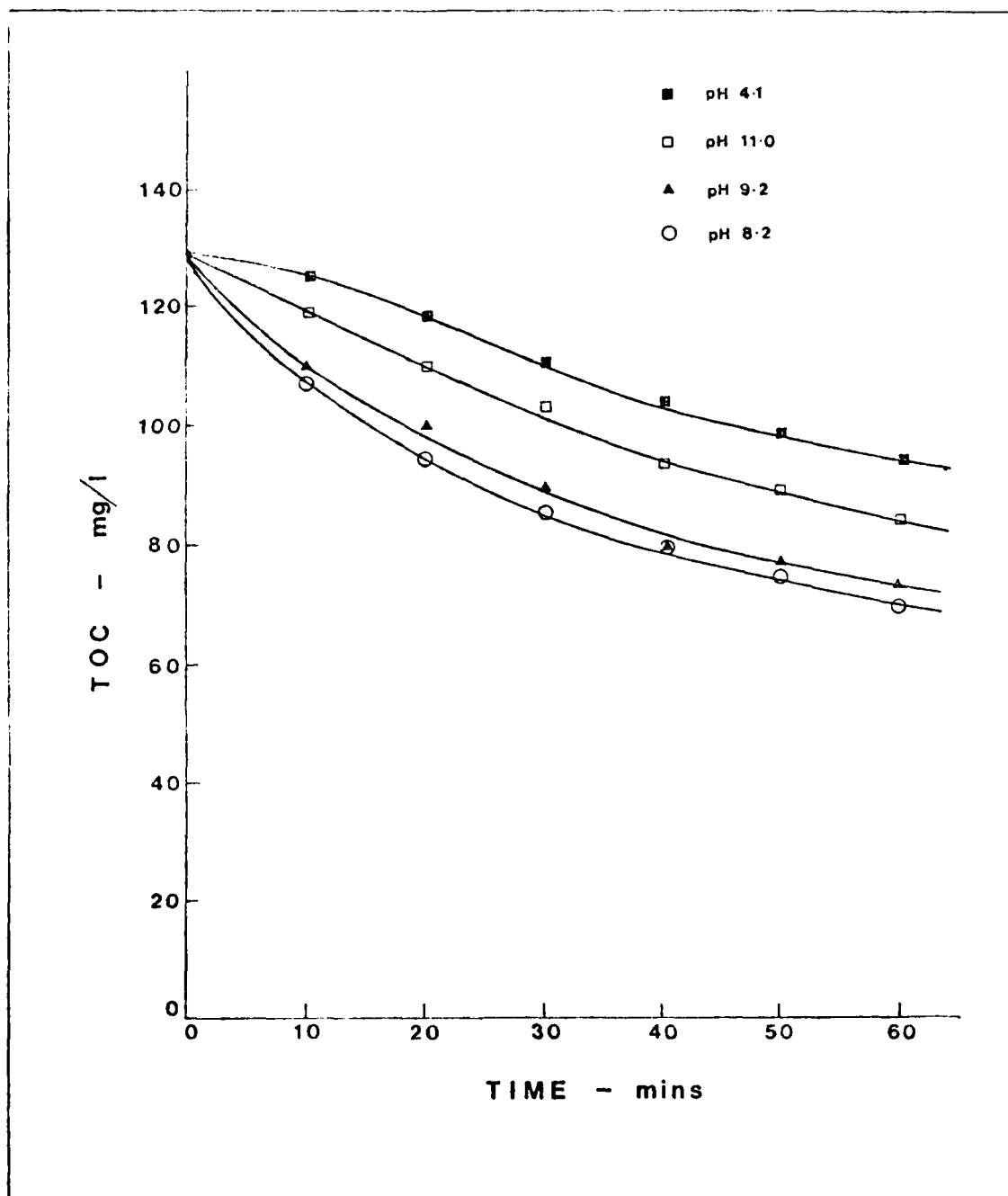Fig. 17 : Percent Change in B O D versus Colour Conversion.

Fig. 18 : Effects of pH on ozonation.

high due to the small concentrations involved, it was found
that at pH 8.2, the dissolved ozone concentration remained at
zero for about 15 - 20 minutes, which indicates that the high
pH also increases the reaction rate of the organics and its
by-products which are now reacting not only with the radicals
but also competing for ozone. Ozone was only detectable in
the exit gas after 15 minutes. This shows that the reaction
was mass-transfer limited for about 15 - 20 minutes and then
reaction-rate limited for the remainder of the reaction when
the slower reaction of the remaining refractory compounds
begins to dictate the reaction rate.

The ozone required to reduce TOC increases when an
ozonation process is performed above pH 9.2. At pH 11.0, a
large loss of ozone will be caused by the accelerated
decomposition of ozone, and the resulting low concentration
of ozone in the liquid will produce a slower reaction.

9.2.8   Colour Removal

The rate of colour removal is very rapid initially,
declining gradually with additional applications of ozone,
Fig.(19).This indicates that the ozone requirements increase
with the progressive oxidation stage of the chromophores.

The changes in COD were measured along with colour
removal. The plot of 'Fractional COD Conversion' versus
'Fractional Colour Conversion' provides evidence that
chemical oxidation occurs simultaneously with colour removal,
Fig.(20). The COD of the sample decreases continuously as
the colour intensity reduces. However, the gradually
increasing slope shows that the COD reduction continues even
though the COLOUR reduction starts to slow down. This is
probably due to :

1.   either only one or two bonds in the dye molecule need to
     be broken to cause a shift in the absorption spectrum, or

2.   the ozone selectively attacks the dye molecule, rather
     than the organics,

It is observed that the disappearance of colour does not
necessarily mean that all those organic compounds that
produces the colour have been oxidised to carbon dioxide and
water. In fact, as will be shown in Section (9.2.9), ozone
preferentially attacks the unsaturated chromophores thereby
decolourising them but does not destroy all of them
completely to carbon dioxide and water. The decolourised
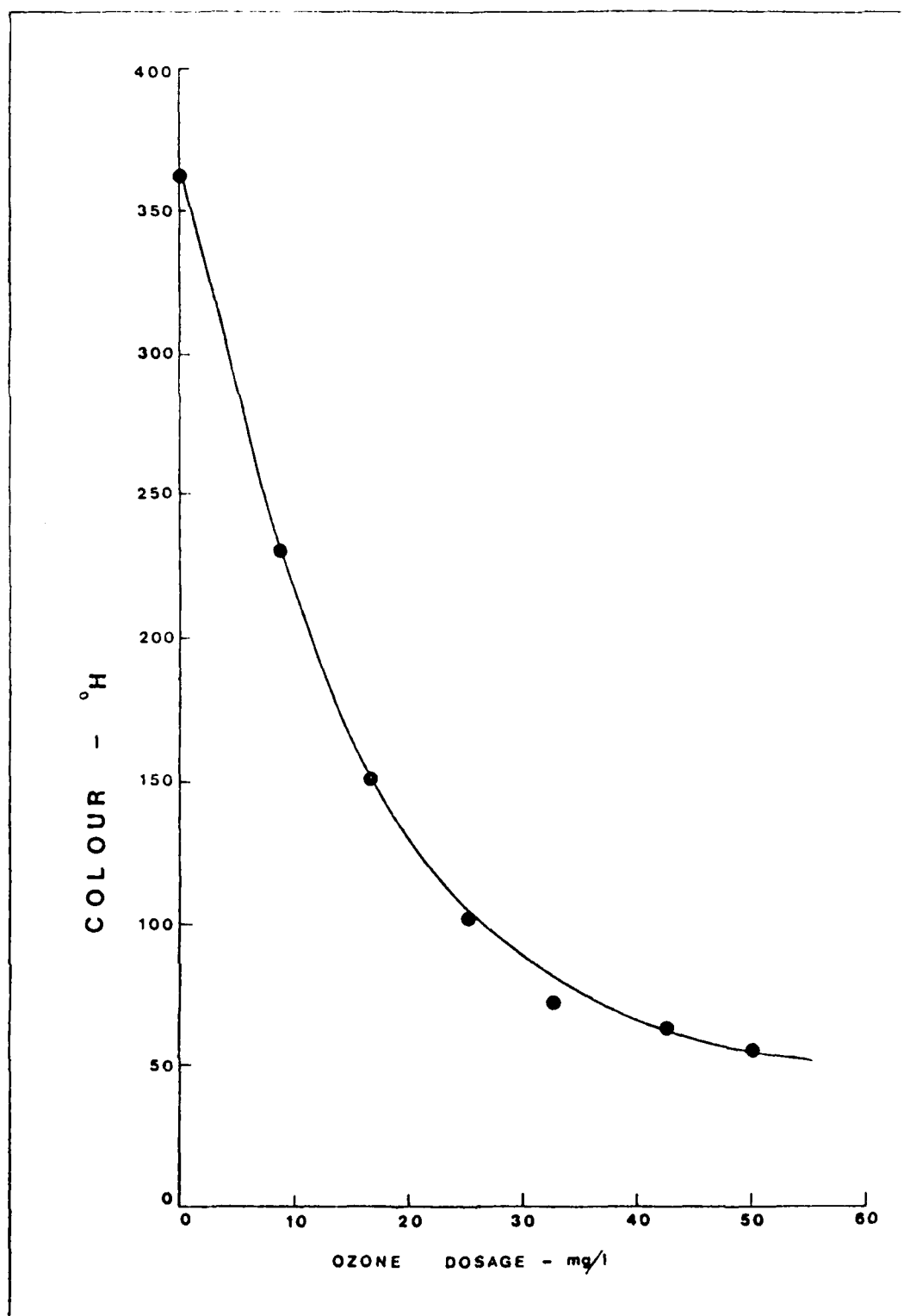effluent still contain a certain proportion of the dissolved

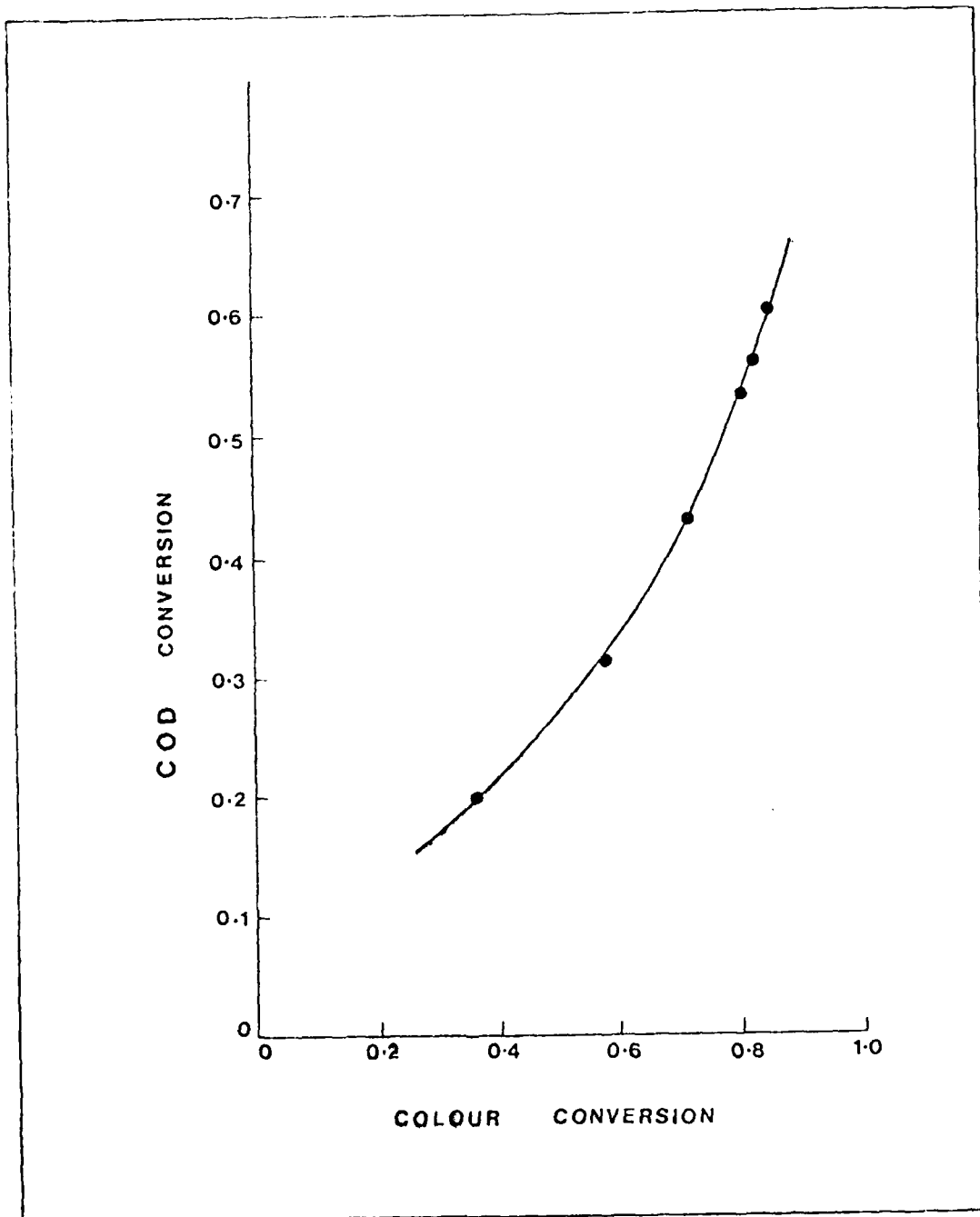Fig. 19 : Effects of ozone on colour removal.

Fig. 20 : C O D Conversion versus Colour Conversion.

organic carbon (which no longer absorb from the visible portion of the spectrum) but is now more readily biodegradable than before ozonation (Section 9.2.6).

9.2.9 Reduction of TOC and UV absorbance

Changes in the sample UV absorbance can be utilised as an indication in changes of organic composition. The 254 nm U.V. light can be used for indicating the number of double bondings in organic compounds.

A plot of fractional changes in TOC and Absorbance, Fig.(21), shows a decrease in both TOC and Absorbance with increased ozone dose, but the reduction in absorbance is much greater than in TOC. The 254 nm UV light is absorbed by unsaturated bonds and therefore this indicates that ozone is preferentially oxidising the double bondings without the organic compounds being completely oxidised.

9.2.10 Return of Colour

Ozonated samples were wrapped up with aluminium foil and kept in a dark place. The samples were tested for return of colour after 24, 48, and 72 hours. Provided that the colour had been reduced to less than 60 H, there was no return of colour even after 3 days.

However, if a very low concentration of ozone was used (3 mg/l) and the final colour of the samples were above 60 H, (120 - 100) H, then a slight increase in colour was observed after 48 hours. This suggests that coloured organic compounds are only partially oxidised by a low dose of ozone to a colourless form and will revert to coloured compounds once they are no longer in an oxidising environment.

For all the other runs (and in all practical ozonation processes), the concentrations of ozone used was in excess of 3 mg/l. A high dose of ozone will bring about a destruction of the structure of the chromophores and prevent a reversion of colour.
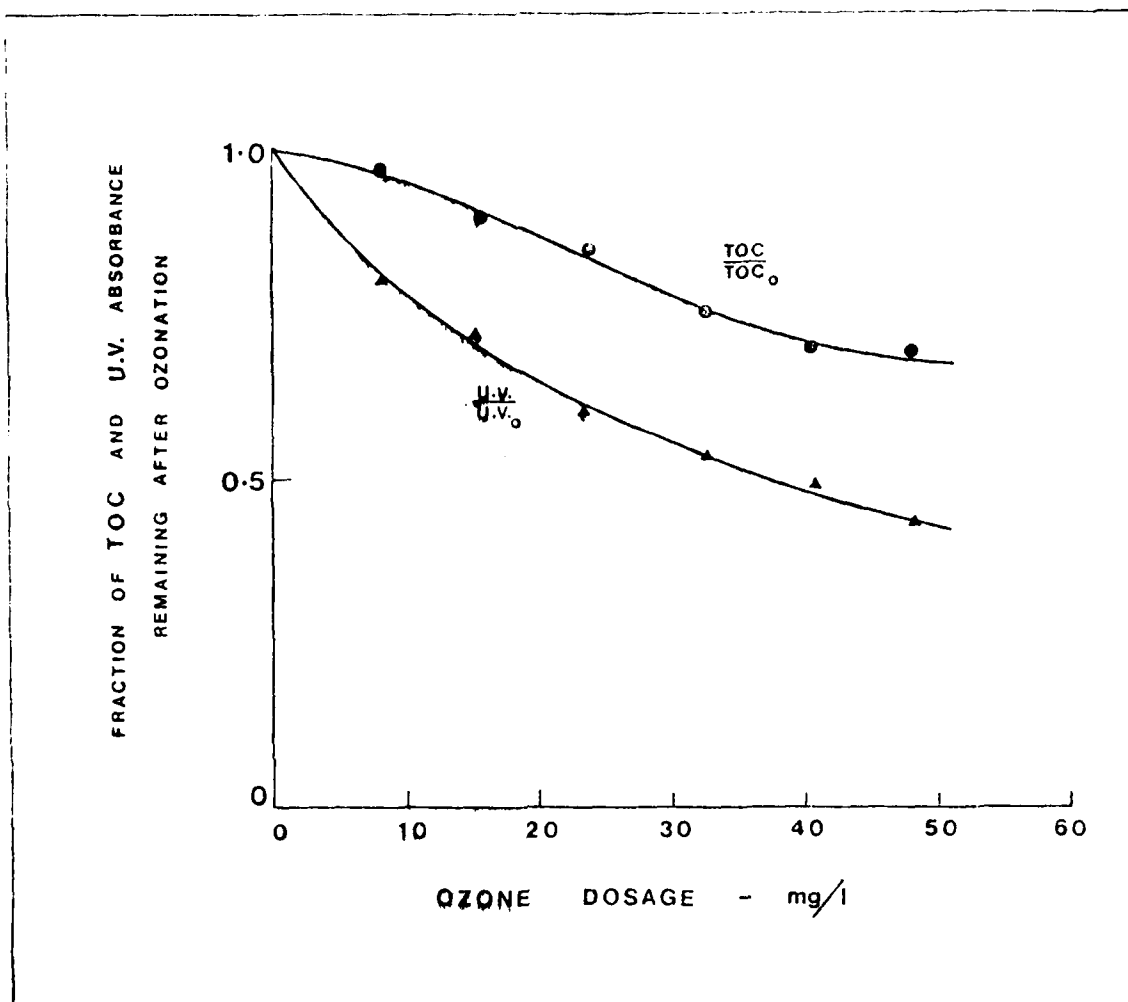
Fig. 21 :   Fraction of T O C and U.V. absorbance
remaining after ozonation
versus
Ozone Dosage.

9.3 OZONOLYSIS OF EFFLUENTS WITH AND WITHOUT SUSPENDED SOLIDS

Obviously the initial values of COD and TOC for a filtered sample (sample 2) would be lower than for a secondary effluent as received, (sample 1). However our data shows that the actual reduction of TOC and COD after ozonation in sample 2 is less than in sample 1. The difference in results for sample 2 (filtered effluent containing no suspended solids) and sample 1 (effluents containing suspended solids) would be due to the interference of suspended solids.

Table (5) shows that the initial COD/TOC ratio of sample 1 would obviously be higher than that of sample 2 because the filtered portion would initially be in a higher oxidation state. However, during the course of the experiment, the COD/TOC ratios of sample 1 decrease faster than the ratios of sample 2, and at the end of the experiment they were even lower than the final ratio of sample 2. This indicates that within the same period of treatment, the unfiltered sample is oxidised more than the filtered sample. The COD/TOC ratio of sample 1 changes by 34 % and that of sample 2 by only 18 %. The only explanation is the fact that ozone must have preferentially attacked the suspended solids. Hence the mechanism of ozone oxidation must be different for particulates and for the soluble portion of the effluent. This raises the question of whether there is an immediate oxidation upon particle-ozone gas contact. Hence, a further experiment was conducted to investigate the effect of disinfection by 'residual ozone alone' and by 'residual ozone plus gaseous ozone', (Section 8.10).

9.4 EFFECTS OF 'RESIDUAL OZONE' AND 'RESIDUAL AND GASEOUS OZONE' ON DISINFECTION

Our results show that the inactivation of coliforms is greater in the presence of ozone gas together with residual ozone. A higher rate of % survival occurs if the inactivation is carried out with residual ozone alone for a given concentration of dissolved ozone, Table (5). This would suggest that the mechanism of oxidation of the particle-ozone gas contact is predominant. To discuss this, a conceptual model for the phenomenon is proposed below.

Table 5 : C.O.D./T.O.C. Ratios

Sample 1 : Secondary effluents as received
i.e, C.O.D. and T.O.C. values are 'TOTAL' values.

Sample 2 : Filtered secondary effluents
i.e. C.O.D. and T.O.C. values are 'SOLUBLE' values.

The difference in C.O.D. and T.O.C. values are due to the
particulates.

Ozone Dosage (mg/l)	Sample 1	Sample 2
	$\frac{C.O.D.}{T.O.C.}$ Ratio	$\frac{C.O.D.}{T.O.C.}$ Ratio
0	2.48	2.00
8.5	2.13	1.91
16.8	1.98	1.84
25.0	1.80	1.77
32.0	1.75	1.72
42.0	1.66	1.69
48.0	1.60	1.64

Table **6** : Effects of 'Residual Ozone' and 'Residual and Gaseous Ozone' on Disinfection

Ozone Dose (mg/l)	Total Coliforms (MPN/100 ml)	
	Residual Ozone	Residual and Gaseous Ozone
0	6.0×10^4	6.0×10^4
0.5	4.0×10^4	2.0×10^4
1.2	2.0×10^4	11.0×10^3
2.1	9.0×10^3	4.0×10^3
4.5	9.0×10^2	5.0×10^2

9.5   A CONCEPTUAL MODEL OF 'RESIDUAL OZONE' AND 'GASEOUS OZONE'
       OXIDATION OF EFFLUENTS WITHIN A TURBULENT THIN
       LIQUID FILM

        In 1974, Rosen et al. (44), suggested a model for ozone
disinfection. He assumed that the rate of reaction of ozone
with bacteria was very fast and that ozone disinfection
occurred by lysis of cells. He also assumed that lysis would
result from a direct contact between the ozone bubble and the
microorganisms. In 1977, Farooq (45) proposed another model
to   explain   the   difference   in degree of inactivation for a
given ozone residual with and without the contact of ozone
gas bubbles.   He found that the presence of ozone bubbles
together with a given ozone residual results in a higher
degree of inactivation than a given ozone residual on its
own. Hence, the effectiveness of ozone disinfection in a
bubble column seems to be limited by the overall rate of
ozone transfer into the bulk liquid rather than by direct
contact with ozone gas bubbles.

        From our results on the effects of ozonolysis of effluents
'with and without suspended solids' and from the results of
the experiments performed on inactivation of coliforms in the
presence of 'residual ozone only' and 'residual plus gaseous
ozone', we can postulate a conceptual model for residual and
gaseous ozone oxidation of particulates within a turbulent
thin liquid film as produced by a rotating disc reactor.

        The oxidising and disinfection mechanism of ozone proceeds
by at least two concurrent methods :

1.   rapid reactions of materials in suspension (and/or
      certain dissolved substances) at the point of contact of
      the gaseous ozone above the liquid layer flowing across
      the disc.

2.   the slower effect of' residual ozone attained over a
      significant period of time.

The   molecules   of the bulk gas phase are continually
transfered to the gas-liquid interface, where they dissolve
into the liquid film. Then the gas molecules diffuse through
this film where the molecules are transported to the bulk
phase by mixing.

        Fig.(22) illustrates the probable ozone concentration
gradient from the gas phase to the liquid film. In the first
instance, let us assume that the liquid layer is flowing
smoothly across a surface. When the ozone gas is in contact
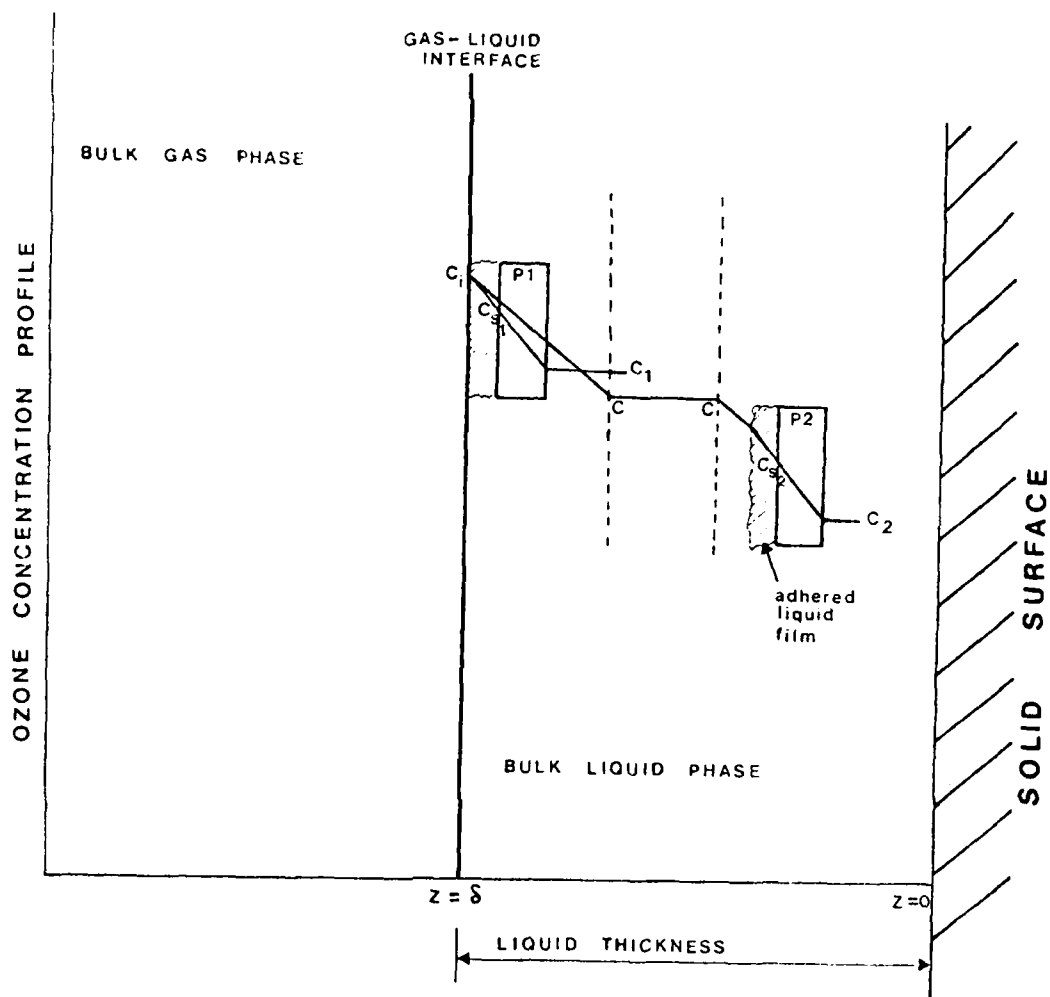
P1 — PARTICLE 1

P2 — PARTICLE 2

C_i — INTERFACIAL OZONE CONCENTRATION

C_{s_1}, C_{s_2} — OZONE CONC. AT SURFACE OF PARTICLES 1, 2.

C — BULK OZONE CONCENTRATION

C_1, C_2 — OZONE CONC. IN PARTICLES 1, 2.

Fig. 22 :   Conceptual Model of Oxidation of Effluents

found within a Thin Turbulent Liquid Film

as produced on a Rotating Disc Reactor.

	1.0	4.5	2.8	2.5
		5.0	3.2	2.2
		5.6	3.6	
			4.0	2.0
	1.1			
				1.8
	1.25	1.4		1.6
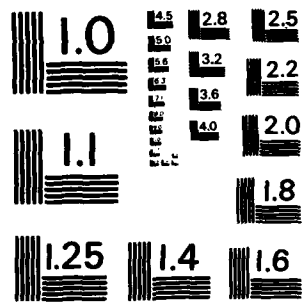
MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

with an effluent particulate, (say, an organism), in the liquid phase, a concentration gradient develops. Because of the very thin liquid layer flowing across the surface, particulates are readily brought up to the gas-liquid interface. (A rotating surface is efficient in promoting this process.). In this region, the concentration of ozone at the surface of the particle wall, C_{s_1}, would be greater than the ozone concentration at the bulk of the liquid, 'C'. The ozone concentration at the surface of any particulates situated in the bulk of the liquid, C_{s_2}, would be lower than that in the bulk of the liquid, 'C'. All particles have an adhered aqueous film, and assuming that the concentration driving force for ozone to diffuse through this adhered aqueous film and the particle wall is the same in both the particles, then the concentration of ozone in a particle located in/near the gas-liquid interface, C_1, would be greater than the concentration of ozone in a particle located in the bulk of the liquid, C_2, since $C_{s_1} > C_{s_2}$. Hence, if the concentration of the bulk of the liquid, 'C', is the same in the runs with liquid phase ozone alone and with gaseous plus liquid phase ozone present, the chances of oxidation is higher if the particle is located in the gas-liquid interface (i.e. in direct contact with the ozone gas) than when it is located in the bulk of the liquid.

However, as shown in Plate (9), the formation of ripples by the liquid on a rotating disc results in an extremely efficient method of simultaneous 'exposure' and 'mixing' of each element of the fluid to the ozone gas as the fluid is being sheared across the rotating disc. Because of the nature of the ripples, turbulence and the very thin liquid layer flowing across the disc, reaction is taking place right at the surface of the gas interface rather than having to diffuse into the mass of the liquid, i.e. $C_{s_1} = C_{s_2}$. The nature of flow of the liquid across the rotating disc is extremely conducive for such a condition to occur.

Hence in our model, we could assume that the rate of oxidation of effluent particulates using a rotating disc contactor is NOT limited by the bulk mass transfer rate of ozone into solution. In other words, if a particulate could be brought into contact with ozone gas, instantaneous oxidation would occur. The possibility of this happening in a bubble column is not as great as in a rotating disc reactor. Also, the importance of mixing, to disperse the aggregates of particles/organisms to be oxidised is extremely important. All these factors dictate the prime design consideration for the treatment of effluents (which obviously would contain particulates). Hence the main objective is to bring all effluent into contact with the ozone gas as rapidly
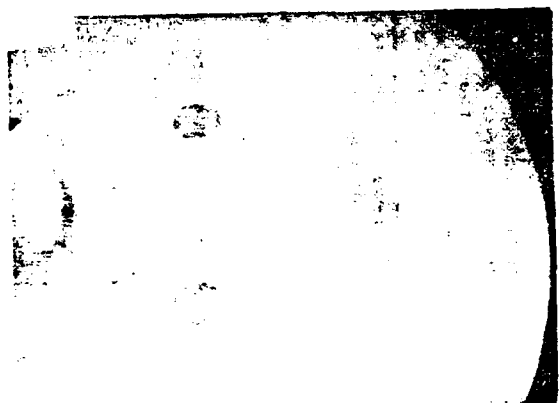
232 rpm

31 cc/s
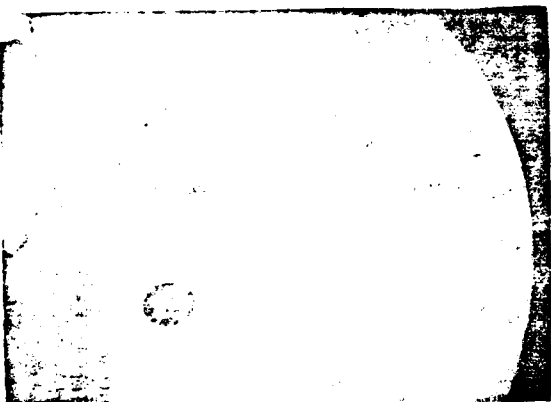
4.17 rpm
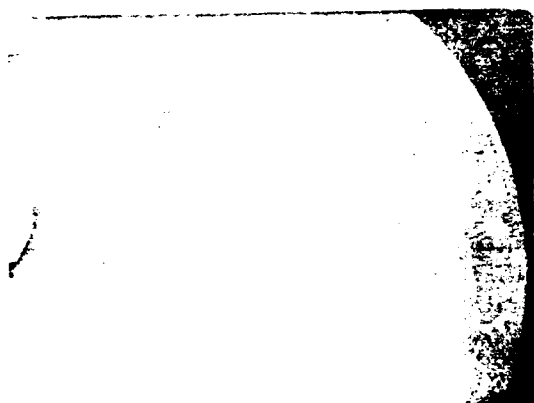
31 cc/s
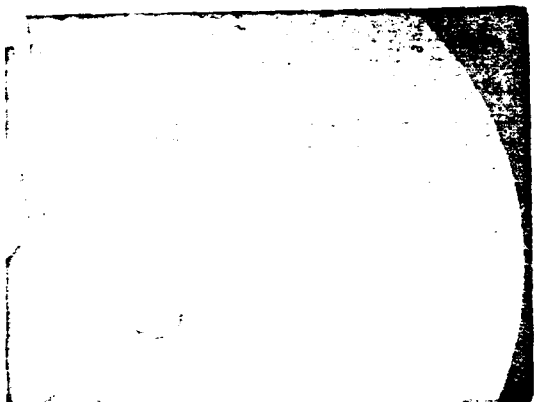
823 rpm

31 cc/s

1120 rpm

31 cc/s

PLATE 9

as possible. This is where the novelty of the rotating disc
reactor comes to play.

9.6   OZONE/ULTRA-VIOLET OXIDATION OF EFFLUENTS

9.6.1   Dissociation with no effluents

The initial run was performed using double distilled water
to find out the degree of dissociation of dissolved ozone
caused by the ultra violet radiation. Without the use of
U.V., the equilibrium ozone concentration was 5.60 mg/l.
When the U.V. lamp was switched on, the equilibrium ozone
concentration dropped to about 4.0 mg/l, Fig.(23). The
decrease in the equilibrium ozone concentration is not
substantial because the U.V. source used is a medium pressure
lamp which radiates predominantly 365 - 366 nm radiation.
The absorption of ozone is most intense with the Hartley
Band, at 250 to 260 nm. This loss of ozone due to
decomposition is not detrimental to the treatment of
effluents since the U.V. enhances the reaction rate (Section
5.0).

9.6.2   Multicomponent Oxyphotolysis

Using COD and TOC as indicators of treatment efficiency,
Fig.(24) shows that the effect of U.V. on multicomponent
effluents is not as dramatic as earlier work, (30), and the
question of why this is so needs to be examined. All
previous work done in the U.S.A. for the past five years were
done with germicidal lamps (254 nm). Our work used a medium
pressure lamp with one predominant wavelength. When you
consider the activation of the organic species, it is
desirable to have lamps ranging from 200 nm to 400 nm.
Obviously if the aim of the treatment is just for
disinfection, then the most practical choice of lamp to use
would be the low pressure lamp (254 nm) . But we are not
solely interested in disinfection. Hence more work needs to
be carried out to investigate the effects of wavelengths on
the 'overall' treatment rate of effluents.

As can be seen from the TOC and COD reduction curves
Fig.(24), the enhancement were not very great, but as
explained above, this could be due to the fact that we were
not using the optimum wavelength or perhaps the desired
'range of wavelengths'. Because the end-point of the TOC and
COD is slightly lower in the case of ozone/U.V. oxidation
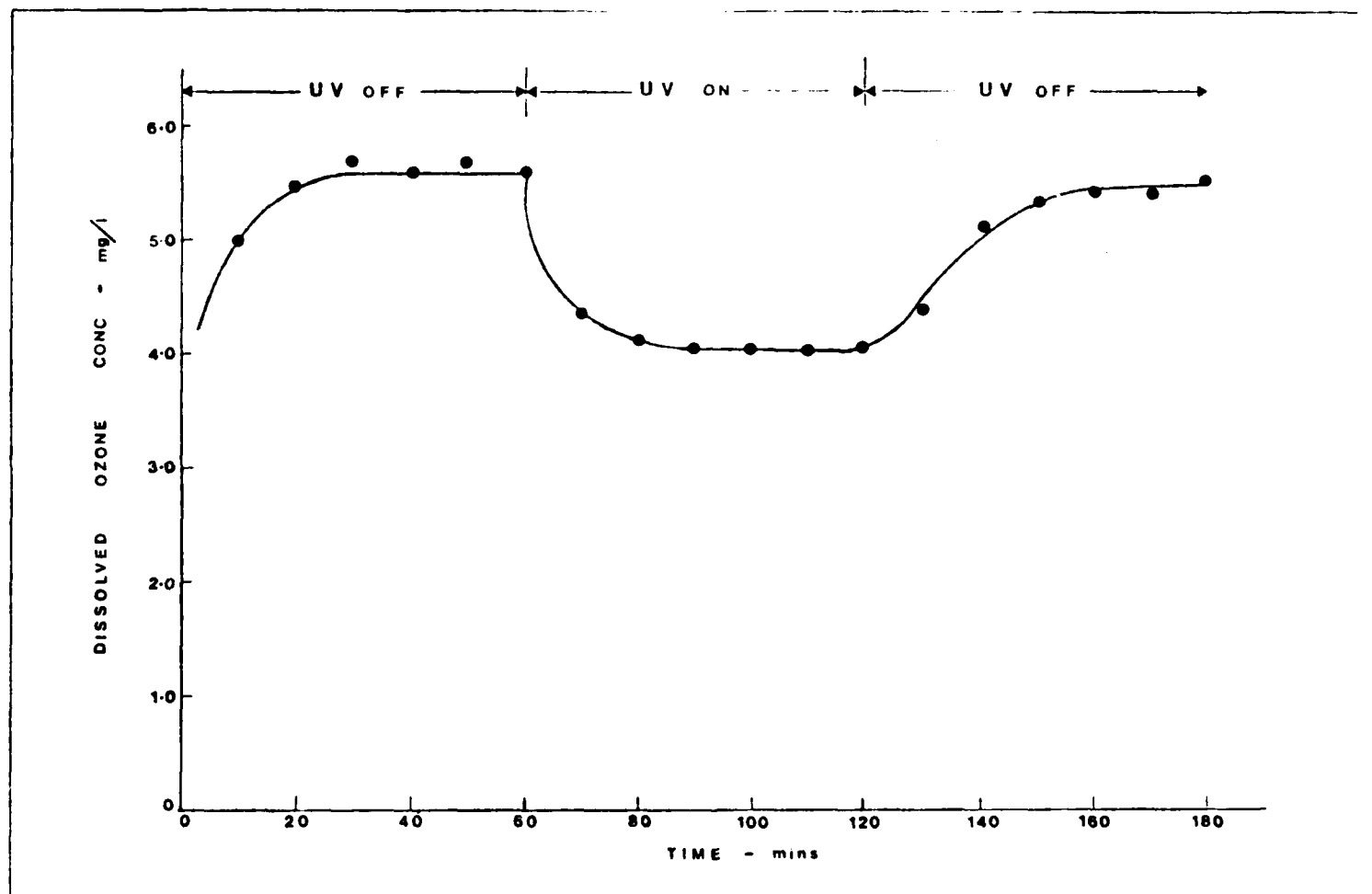than in the case of ozonolysis alone, it is suggested that

Fig. 23 : Dissolved Ozone Concentration with and without U.V. Irradiation.

oxyphotolysis can decrease the ozone demand for TOC and COD reduction.

Extreme care was taken to ensure that the whole system was operating isothermally (20 $^\circ$C) so as to ensure that any differences in results obtained from these runs are due to the effect of U.V. alone and not the effect of an increased in temperature due to the presence of the U.V. source. The data-logger proved extremely useful in continuously scanning the temperature at different points of the rig.

9.6.3 Single component Oxyphotolysis

The multicomponent nature of the effluents could 'mask' the effect of the U.V. Because of this, the rotating disc reactor was tested on a typical single component effluent.

Only low concentrations of phenol were used because these are the ranges found in practice; thus the ozone concentration used in these tests were correspondingly lower. Work was carried out to compare the effectiveness of the reactor compared with a standard diffusion vessel. Fig.(25) shows that, for the same effective dose rate and residence time, the rotating disc reactor utilises ozone more efficiently. When U.V. is applied, Fig.(26) shows that the same dramatic effect achieved by earlier workers (30) is observed. This result suggests that the multicomponent effluent has a wide spectrum of absorption bands which are not matched by the lamp used. It is possible to achieve complete treatment with a single component, but the design of a multicomponent U.V./Ozone reactor system will depend on the effluent used.
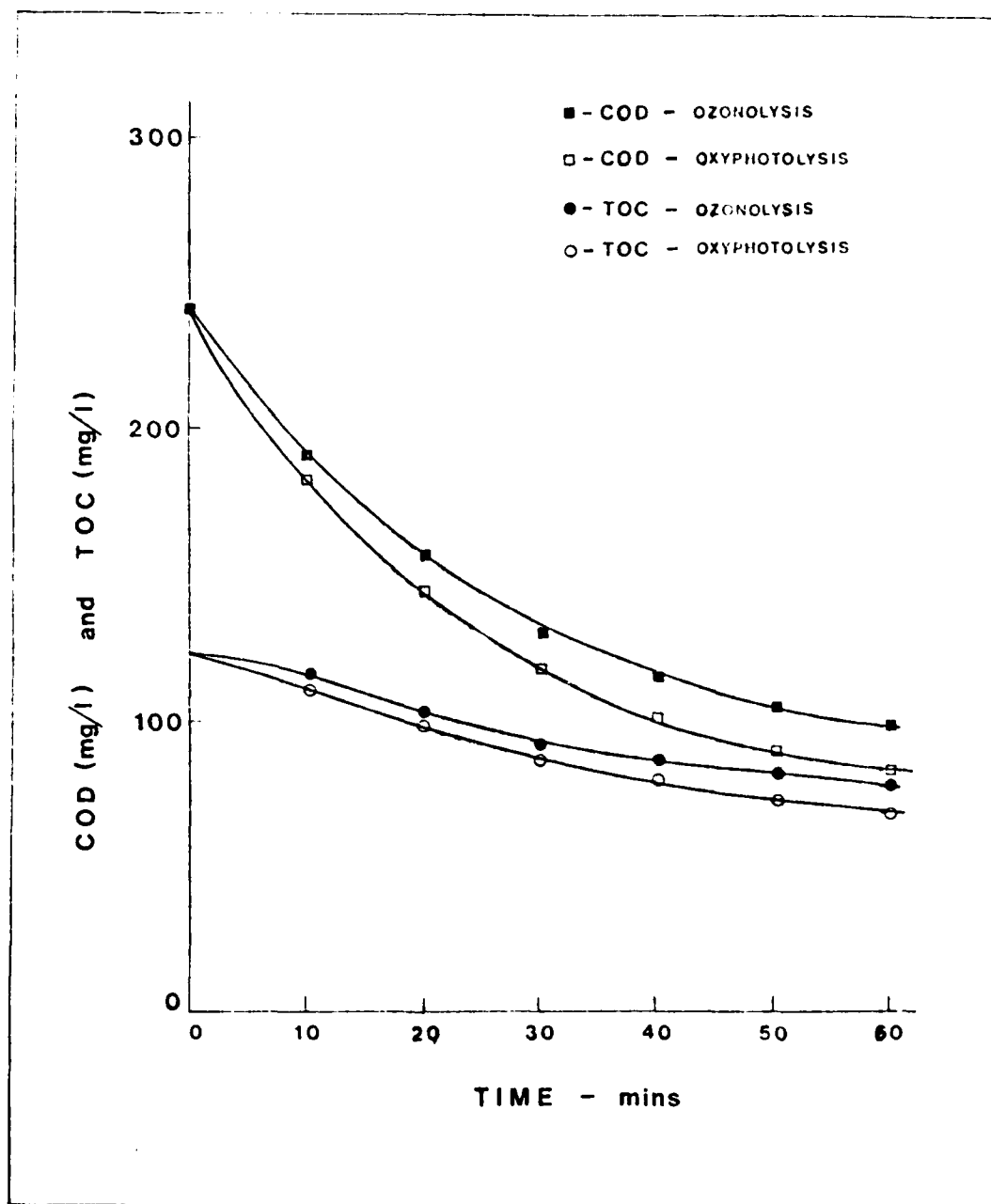
Fig. 24 : **Effects of oxyphotolysis on C O D and T O C.**
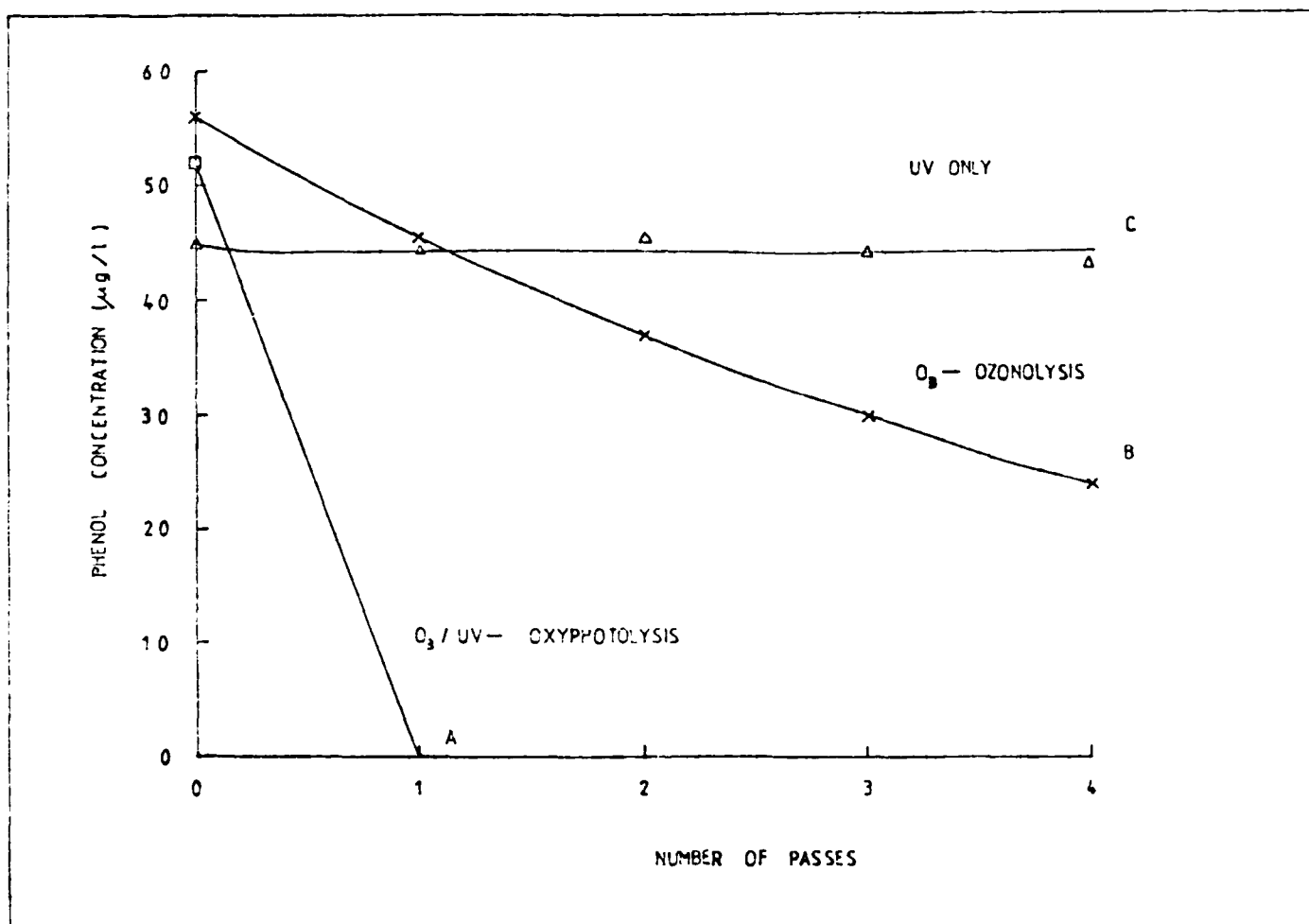
Fig. 26 : Comparison of Oxyphotolysis and Ozonolysis(Initial O₃ conc.= 0.054 mg/l)

10   CONCLUSIONS

10.1   MASS TRANSFER TO THIN LIQUID FILMS USING A ROTATING DISC REACTOR

10.1.1   Distribution Coefficient

The results of the mass transfer and distribution coefficient allow one to predict the true dissolved ozone concentration in an absorption equipment. The distribution coefficient for water at 20 °C is 0.24. The 'fractional' distribution coefficient for a gas/water volume ratio of 1:2.50 is 0.21 for the contactor used in this work.

10.1.2   Mass Transfer Coefficient

The experimental mass transfer coefficient is found to be 4.1×10^{-4} m/s while the value of the mass transfer coefficient calculated using similar physical operating conditions from an empirical formula for the hydrodynamics of the rotating disc reactor is 4.7×10^{-4} m/s. The slight discrepancies in results on the mass transfer coefficient is due to the difficulties in measuring accurately low concentrations of dissolved ozone, and also the impossibility of preventing ozone decomposition in water. The empirical design equation used was developed from the physical absorption of oxygen by a rotating disc reactor. Because of its high reactivity, experiments with ozone have shown that there is a slight decomposition even with double distilled water. Within experimental errors, the mathematical relationship obtained from previous work for the physical absorption of oxygen in a rotating disc reactor has been shown to be applicable to the 'physical' absorption of ozone in pre-treated double distilled water.

10.2   THE ROTATING DISC REACTOR

The above considerations, and measurements making a direct comparison using a single component effluent (phenol), suggests that the rotating disc reactor is more efficient than conventional techniques (i.e. bubble columns). The advantages of the rotating disc reactor in effluent treatment over conventional mass transfer equipments are :

1. Low cost :- because of small size of contactor and reductions in ancillary equipment. The full capital cost

would need to be evaluated.

2. Low energy consumption :- for the high rates of gas absorption a high energy efficiency of 1.50 kg/KWh of oxygen is achieved with a single disc.

3. Efficient mass transfer :- the mass transfer coefficient for ozone is double the best reported value.

4. Simple design :- flexibility to allow the variations of operating parameters.

10.3 PH AND REACTION MECHANISM

Experiments performed with double distilled water showed that a higher steady state dissolved ozone concentration can be attained at a lower pH and vice versa. There is an increase in the rate of dissolved ozone decomposition with pH values and the rate constant increases with pH values.

The reaction conditions for effluent treatment can be chosen to favour either a 'direct reaction' of molecular ozone, or a 'free radical' reaction using the free radicals available either from the effect of the pH dosing additive or from the dissociation of molecular ozone using U.V. irradiation. Because of this, there is an 'optimum' pH value and an 'optimum' range of wavelengths. For the typical refractory bearing effluents used in this work, the optimum pH was found to be pH 8.2. More work need to be carried out to determine the desired range of wavelengths.

10.4 GAS/LIQUID INTERFACE REACTIONS

For the oxidation of effluent particulates which are not inert (say, bacteria), it has been shown that gaseous ozone will preferentially attack them. Because of its selectivity, ozone is an efficient disinfectant since its consumption by the other contamninants is a comparatively slow process. On the contrary, if one is treating refractory organic impurities remaining after conventional secondary treatment, then conditions should be chosen which favour a preceeding decomposition of ozone leading to highly reactive radicals which react rapidly with the different types of dissolved organics. In the rotating disc contactor, every element of liquid can be brought into contact with the gaseous phase for particle oxidation or disinfection and simultaneous liquid phase reactions occur. Hence, the reactor is conducive for promoting both a 'direct reaction' of molecular ozone, or a

'free radical' type reaction.

10.5   EFFLUENT TREATMENT

It was found that ozone in conjunction with this apparatus was particularly useful for tertiary treatment. The use of ozone as a tertiary treatment process for our effluents results in reductions in the BOD, COD, TOC, colour, turbidity, suspended solids and biotreatability of the effluents. Disinfection of the effluents occur simultaneously.

10.6   OXYPHOTOLYSIS

Earlier published work on single component refractories showed spectacular oxidation in the presence of ozone and ultra violet. This has been confirmed in this work using the rotating disc reactor. However, with the multi-components used in this study, the results from this study have shown that ozone/U.V. oxidation is only slightly more effective than ozonolysis alone. It is suggested that this is because the U.V. lamp available was not of the optimum wavelength. Much more work is required before full-scale operation can be envisaged on multi-component effluents.

10.7   RECOMMENDATIONS FOR FUTURE WORK

1.   The work described in this report is on smooth rotating surfaces. Hydrodynamic studies with non-reactive gases carried out in these laboratories on non-smooth rotating surfaces have shown great improvements in the mass transfer coefficient. Further work on effluent treatment is needed to investigate the use of 'cartridges' of such discs (rather than a single disc) which will allow throughputs of up to 20.0 litres/sec.

2.   Ultra violet radiation attenuates very rapidly as a function of distance in a liquid. Hence in our present experimental set-up, it can be presumed that the reaction is occuring primarily in the liquid film surrounding the quartz wall housing the U.V. source. Therefore, rather than having the U.V. source in a separate photochemical reactor, the U.V. lamp could be incorporated into the rotating disc itself, thereby allowing liquid containing ozone to be swept past the thin film reaction surface surrounding the ultra violet source. The ozone is decomposed, primarily forming the hydroxyl radical (Section 5.0) which is more reactive than ozone. The

half-life of the hydroxyl radical is about 1×10^{-4} seconds, whereas the half-life of ozone in the liquid phase is measured in minutes. Because of this ozone decomposition in the liquid phase, there exists a greater concentration gradient between the gas and the liquid phases. This concentration gradient provides the driving force for the transfer of more ozone into the liquid phase. As a result of these two effects occuring on the disc, the oxyphotolysis process can be made to utilise ozone more economically and more efficiently. However, it should be noted that placing the U.V. source in the gas phase will produce premature dissociation of ozone which is not beneficial. Similarly, if the lamp is housed within the disc, care should be taken to ensure that the U.V. radiation be prevented from penetrating through the liquid into the gas phase.

3. More sophisticated methods of ozone analytical method should be employed for measuring the radial ozone concentration of liquid on the disc itself. This can be achieved by having embedded ozone electrodes on the disc to monitor the concentration profile of the liquid across the disc. With existing techniques, it is not possible to monitor ozone as a function of liquid depth.

4. A continuous ozone monitoring instrument for measuring liquid and/or gas concentration would provide more accurate data on ozone concentrations.

5. More work should be done to investigate the optimum U.V. intensity to be used and the effect of the spectrum of the U.V. light on the oxidation rate of multi and single component refractories.

6. Further attempts to generate ozone at the gas/liquid interface using improved pulsed power supplies in conjunction with rotating discs are worthy of investigations.

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Appendix A

VOLTAGE-CURRENT CHARACTERISTICS OF ELECTRICAL DISCHARGES

The experimental set up used to investigate the characteristics of electrical discharges are shown in Plates Al and A2.

A-0.1   Point-to-Plane Model

The apparatus used to investigate the voltage-current characteristics of a Point-to-Plane discharge consists of two concentric hemispherical aluminium cups, the external cup acting as a shield against any stray capacitance from the surrounding and the inner cup acts as the receptor for discharge current. Both cups have smooth curved rims to reduce its electric fields.

The discharge current was measured by connecting the inner cup to a microammeter. To observe the waveform of the current, an oscilloscope was connected across the resistor attached to the inner cup. Stainless steel needles with different radius of curvature were used as the point discharge source. The following parameters were investigated :

1. "Onset" corona voltage for different radius of curvature.

2. Current-Voltage characteristics.

3. Amplitude-Voltage relationships.

4. Frequency-Voltage relationships.

5. Frequency-Current relationships.

The onset voltage for the various needles were recorded as the minimum treshold voltage required to cause the oscilloscope to display a signal. Fig.(Al) shows that the onset voltage increases with the radius of curvature of the needles. This is due to the decrease of electric field with increasing radius.

Fig.(A2) shows the current-voltage characteristics. The first three electrodes have almost identical current-voltage characteristics.

The pulse amplitude decreases with increase in voltage, Fig.(A3). The needles with larger radius of curvature have a larger pulse amplitude.

The frequency of the pulses increases with voltage (Fig.A4) and the increase is greater for needles with smaller radius of curvature.

The frequency of the pulses increases with current and again, the increase is greater for the sharper points (Fig.A5).

A-0.2   Coaxial Model (wire-in-cylinder).

The apparatus used to investigate the discharge characteristics in the coaxial model is shown in Fig.(A6). It consists of two concentric cylinders, the outer cylinder acting as a shield for the inner cylinder from any stray capacitance. Both cylinders have smooth curved rims to reduce its electric fields. The shield was earthed. Wires of various diameters were used in this experiment.

The current-voltage characteristics for different wire diameters is shown in Fig.(A7). Fig.(A8) shows that the thicker wires have a higher onset voltage. Fig.(A9) shows the relationship between the current and the wire diameters for different applied voltages.

The current-voltage characteristics for different lengths of wire is shown in Fig.(A10). It shows that the discharge current increases with the length of the discharge wire. This is due to the increase in emission sites. Fig.(A11) shows the relationship between the current and different wire lengths for different applied voltages.
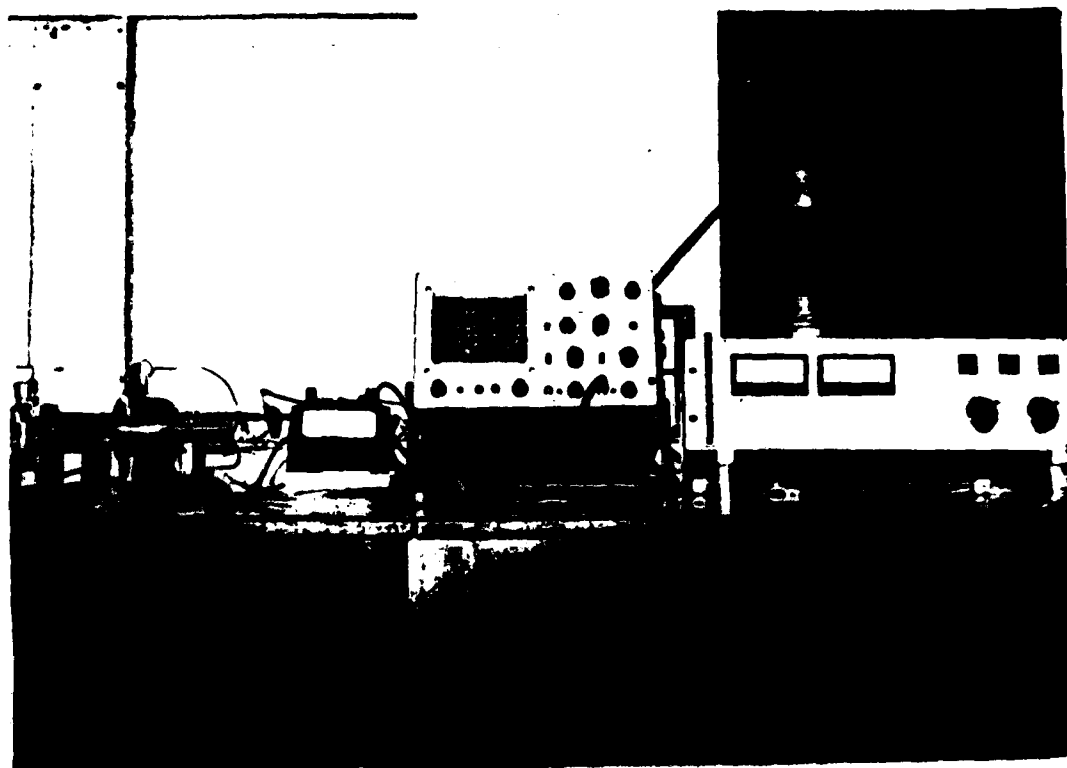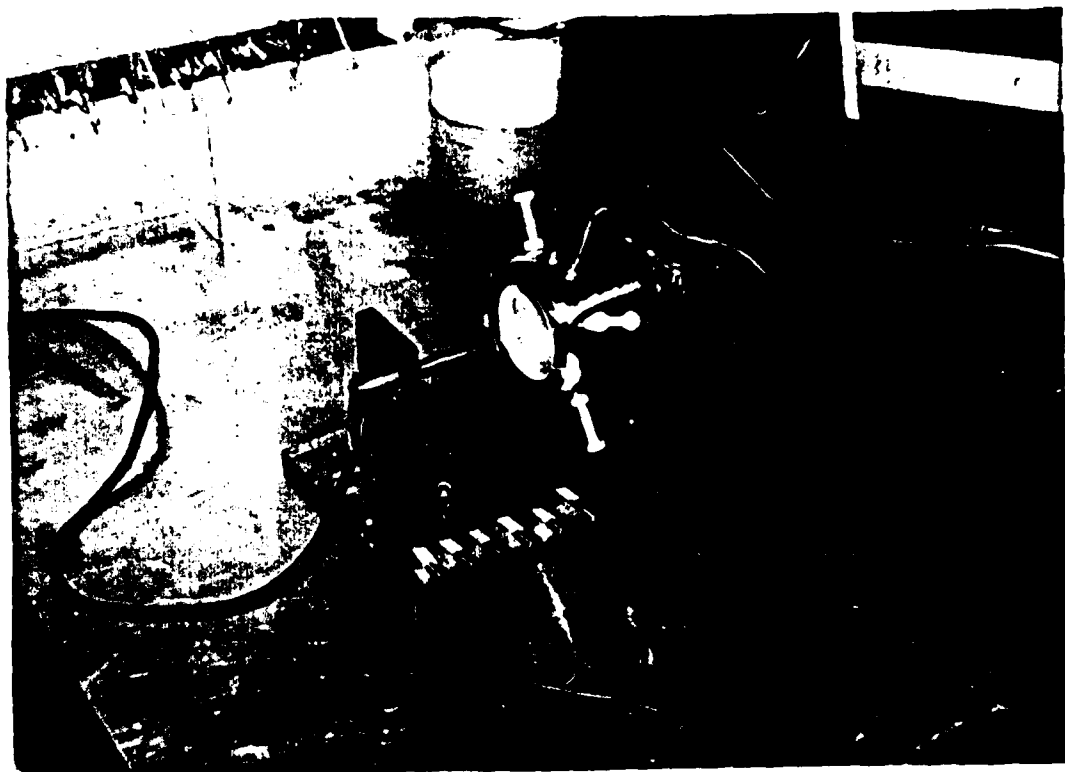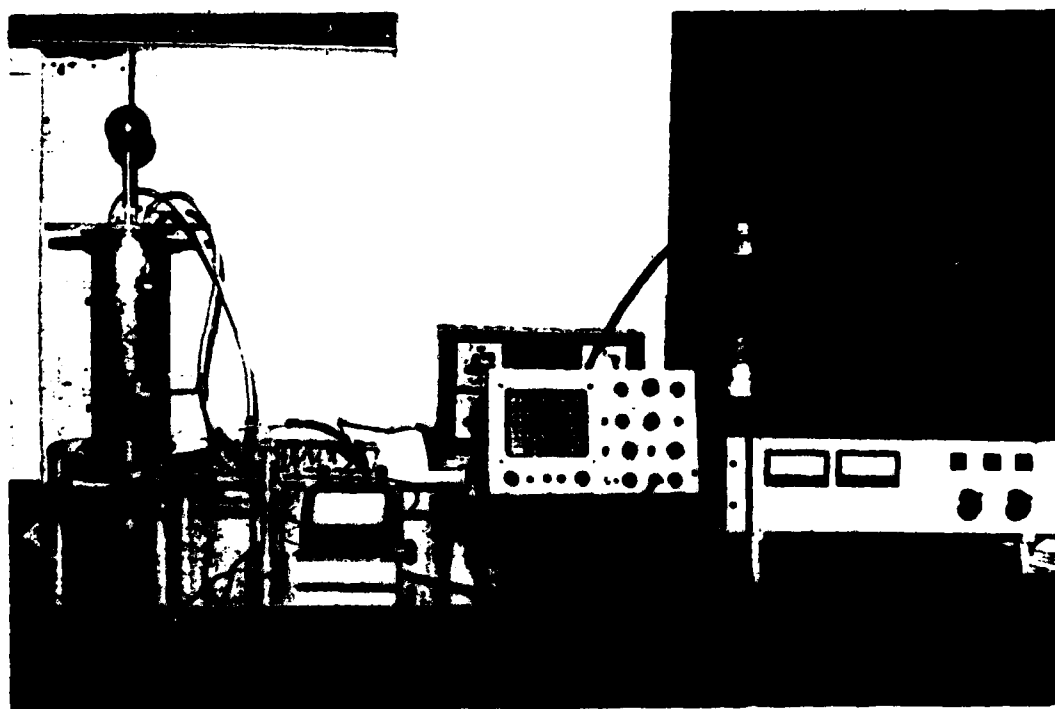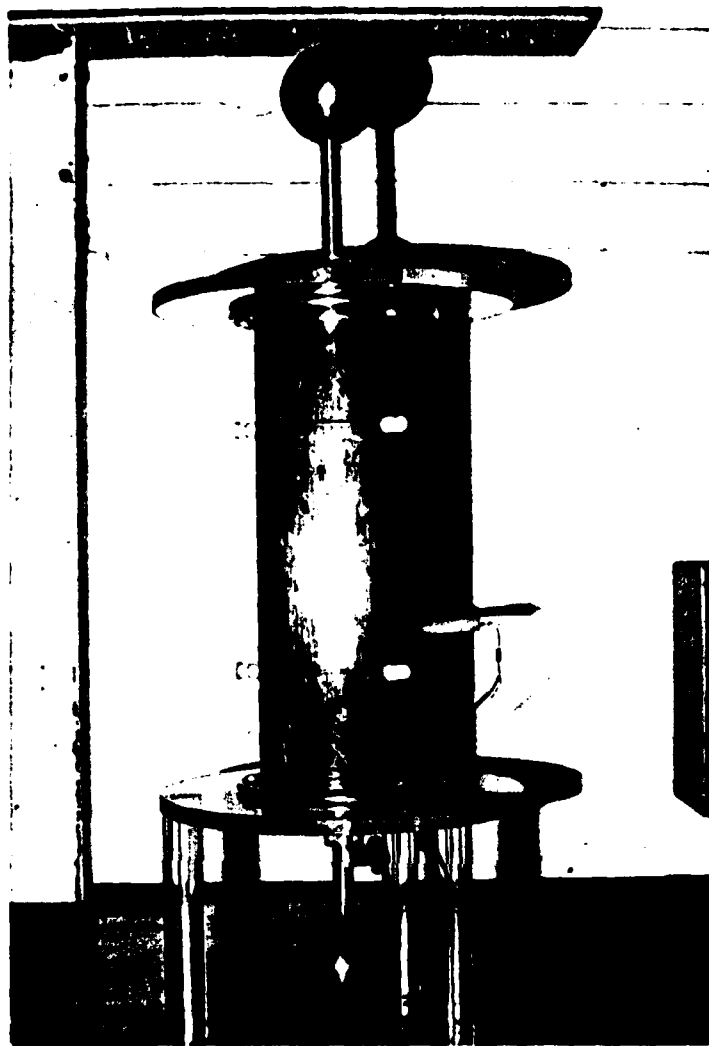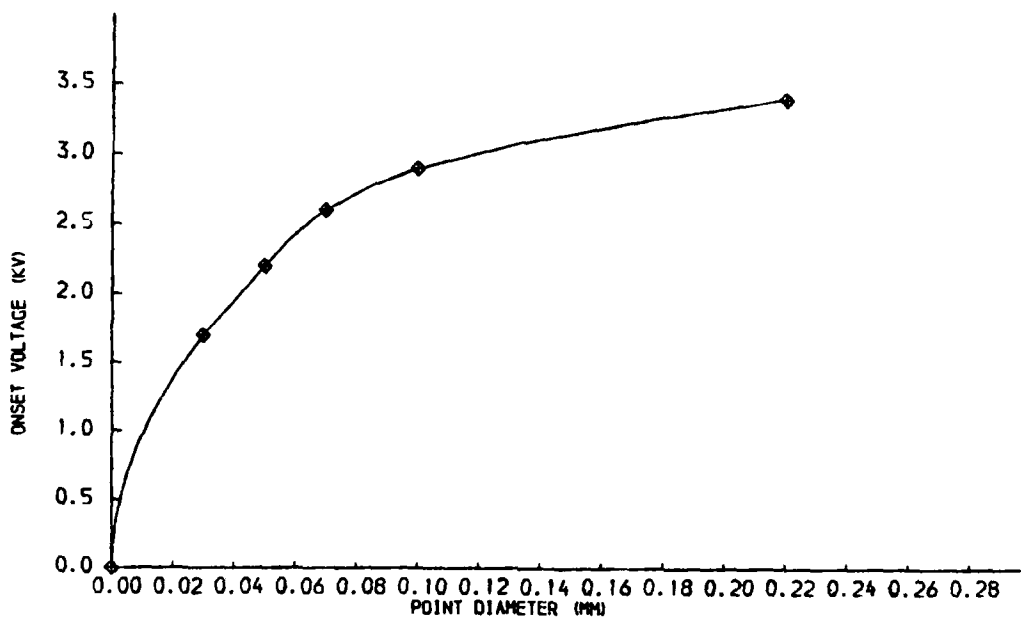
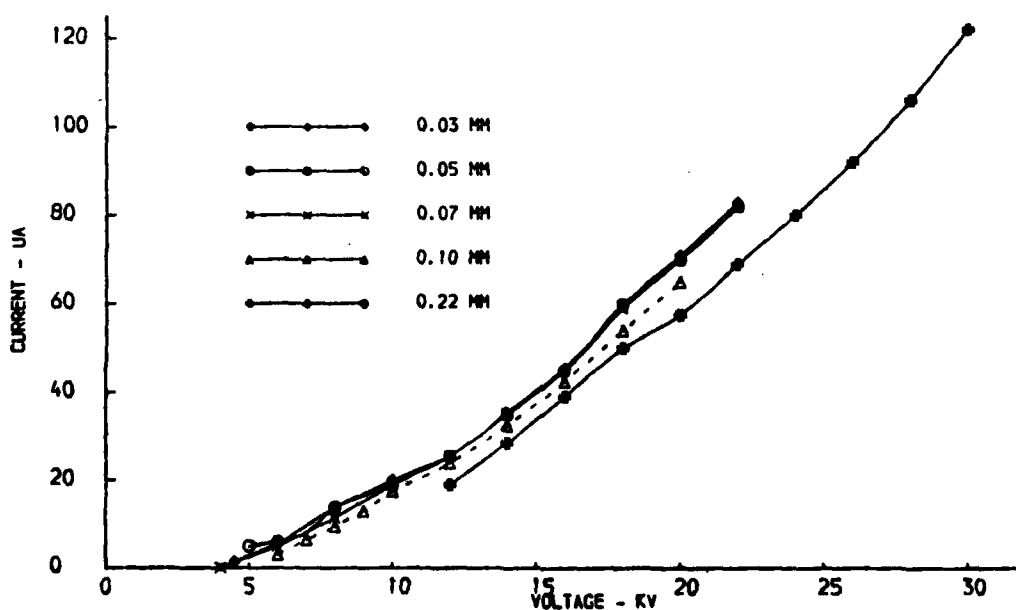FIG. A1: ONSET VOLTAGE VS. POINT DIAMETER
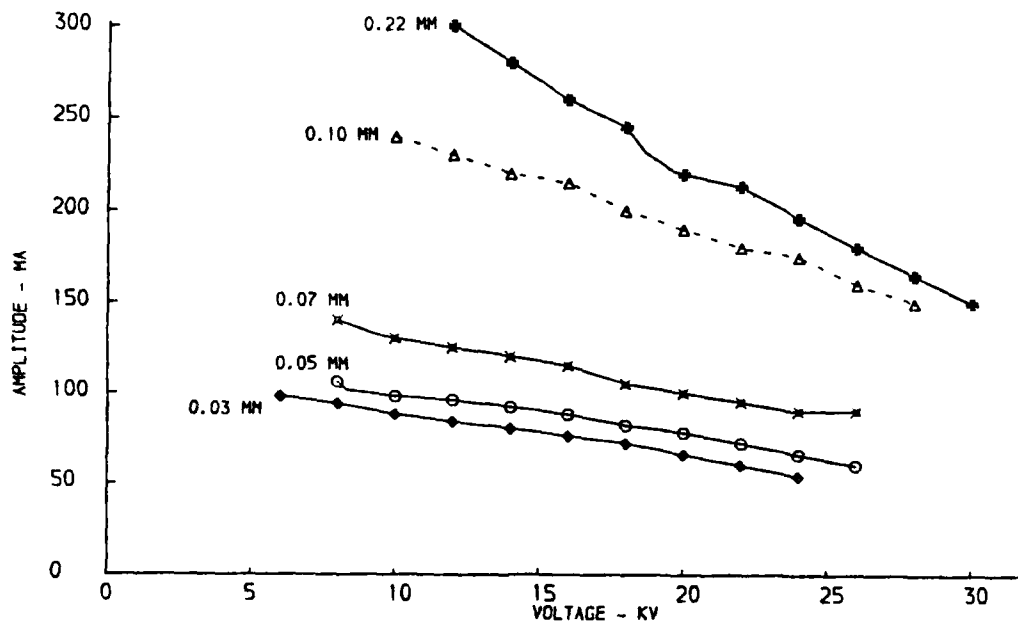

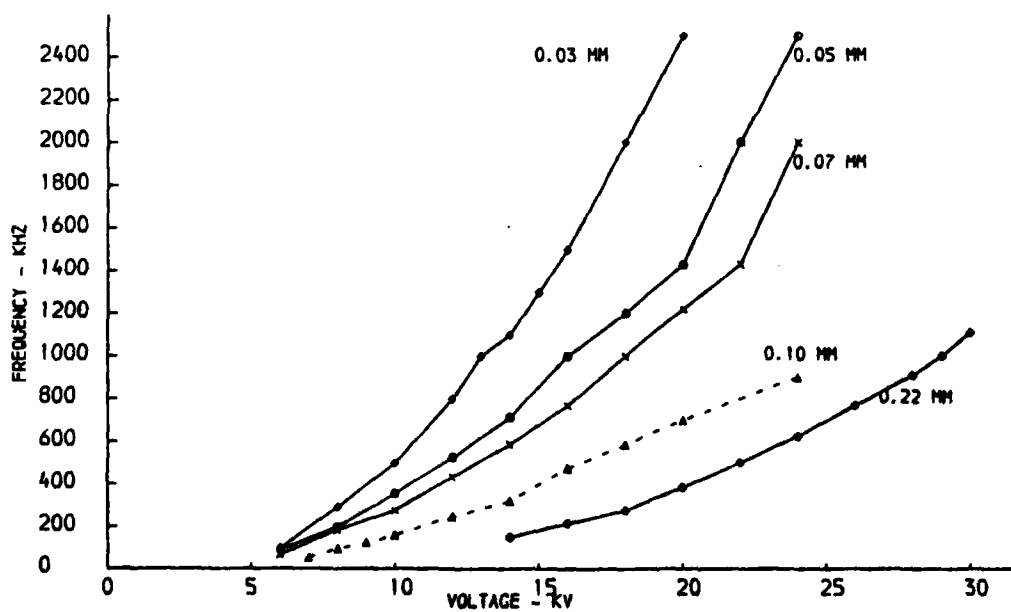FIG. A2: CURRENT VS. VOLTAGE

FIG. A3: AMPLITUDE VS. VOLTAGE
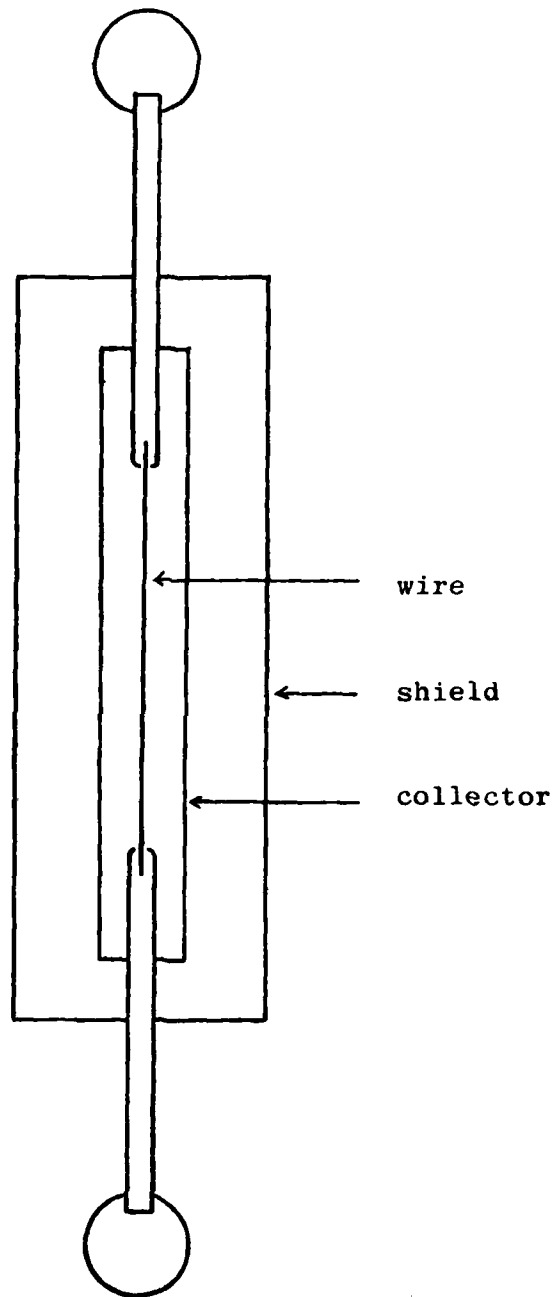

FIG. A4: FREQUENCY VS. VOLTAGE

wire

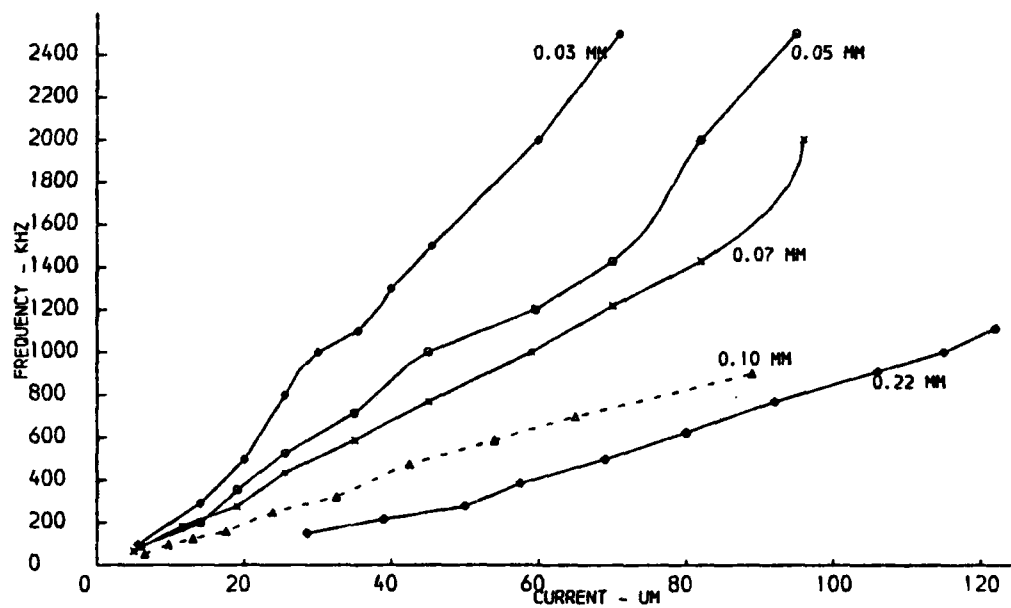shield

collector

Fig. A6 : Wire-in-Cylinder Apparatus

FIG. A5: FREQUENCY VS. CURRENT
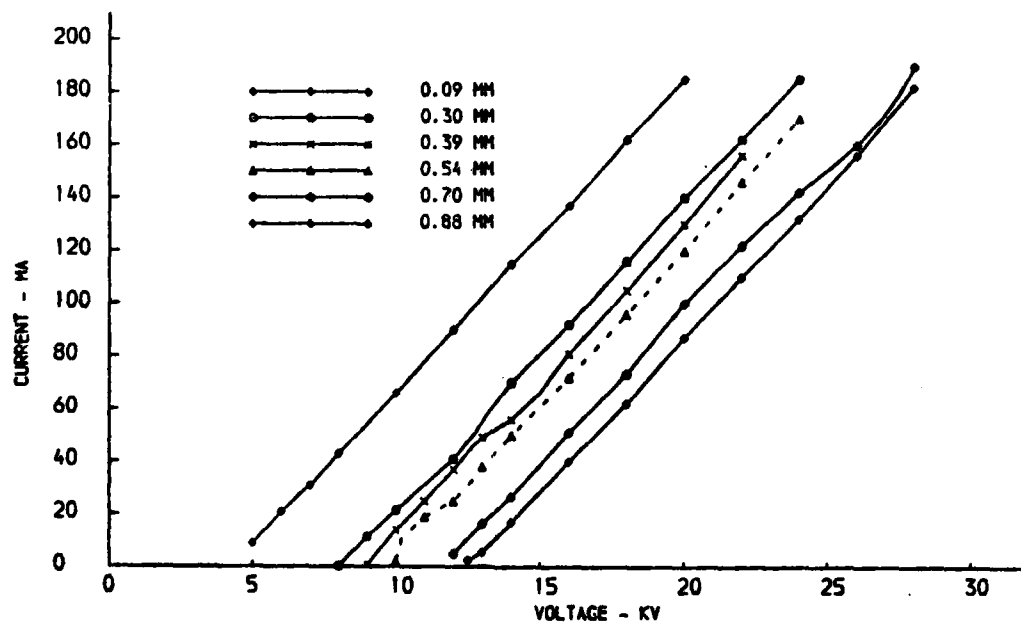

FIG. A7: CURRENT VS. VOLTAGE
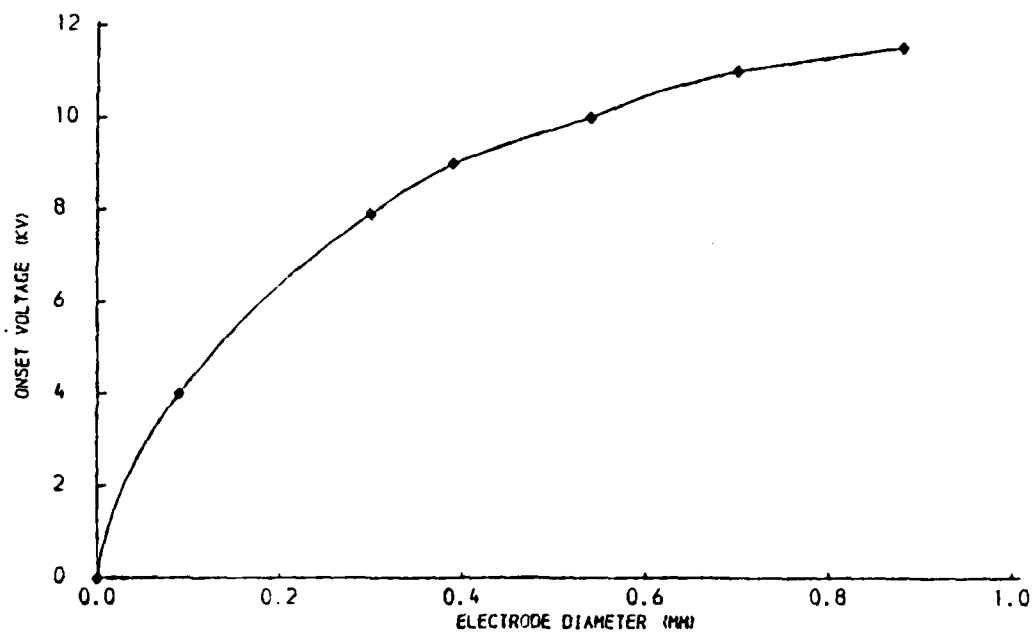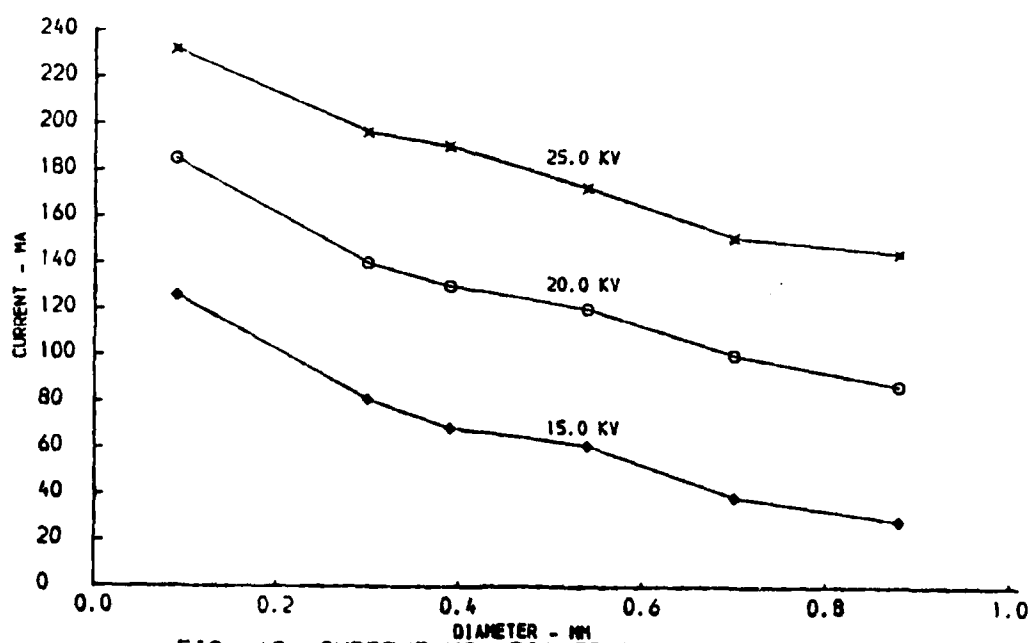
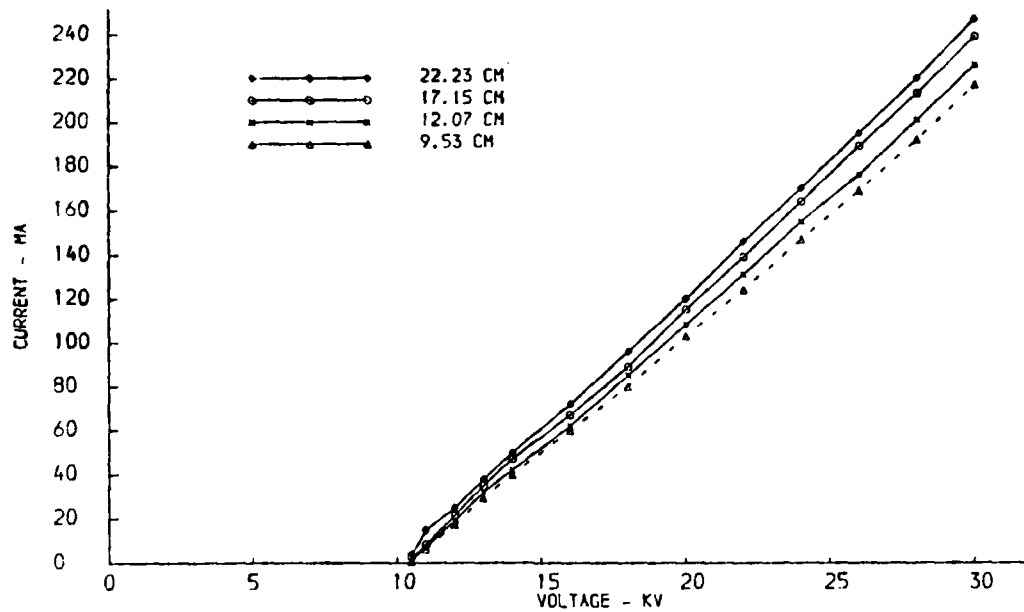FIG. A8: VOLTAGE VS. ELECTRODE DIAMETER

FIG. A9: CURRENT VS. DIAMETER

FIG. A10: CURRENT VS. VOLTAGE

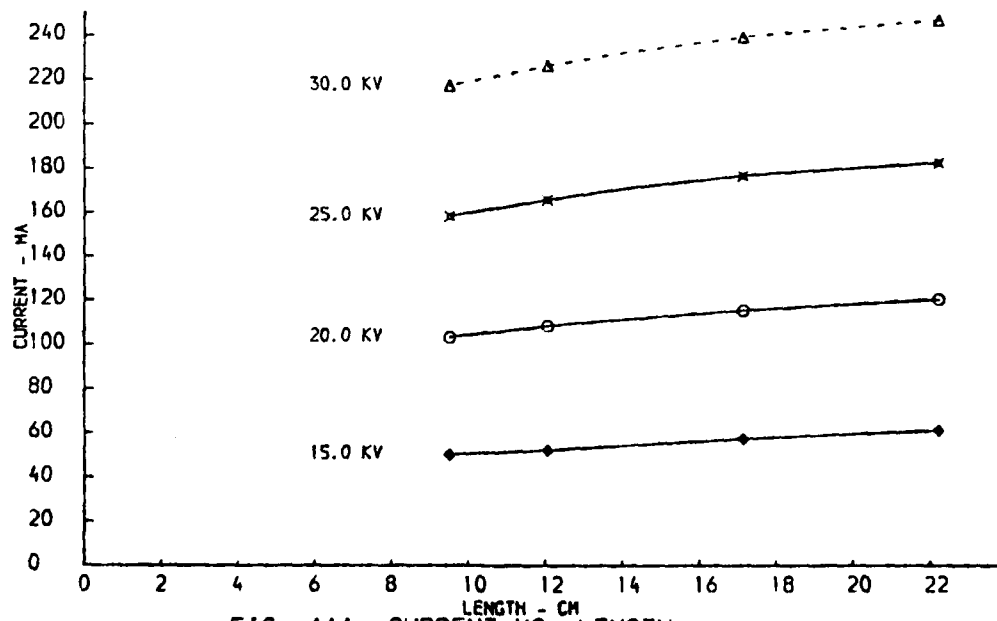FIG. A11: CURRENT VS. LENGTH

Appendix B

Calculation of the Mass Transfer Coefficient using the
empirical correlation for the Rotating Disc Reactor

The mass transfer coefficient can be calculated from:-

$$= 4.76 \times 10^{-3} \, Re^{0.68} \, Ta^{0.37} \, R^{*-0.53}$$

where $Re = \dfrac{Q}{r \, v}$

$Ta = \dfrac{w \, r^2}{v}$

$R^* = \dfrac{r}{r_i}$ where r = radius of disc
                           r_i = distributor plate radius

and $Sh = \dfrac{k_L \delta}{D}$ where D = Diffusivity
                              δ = film thickness

The diffusivity of O_3 in water can be predicted from the Wilke
and Chang correlation for dilute solutions:-

$$D_{AB} = \frac{7.4 \, (10^{-8}) \, (K M)^{0.5} \, T}{(v \, v^{0.6})}$$

where D_{AB} = diffusivity of A in dilute solution in solvent
B (cm^2 / sec)

M = molecular weight of solvent = 18 g/mole

T = Temperature $^\circ K$ = $293^\circ K$

v = solution viscosity (cp) = 1 cp

V = solute molar volume at the normal boiling point = 35.45 cm^3/g mole

K = association parameter for the solvent, eg. for water $x = 2.6$

Solving:

$$D_{O_3} = \frac{7.4 \times 10^{-8} (2.6 \times 18)^{0.5} \times 293}{1 \times (35.45)^{0.6}}$$

$$= 1.74 \times 10^{-5} \; cm^2/sec$$

$$Sh = 4.76 \times 10^{-3} \; Re^{0.68} \; Ta^{0.37} \; R*^{-0.53}$$

$$Re = \frac{Q \,(m^3/s)}{r \,(m) \, v} = \frac{0.00003}{0.19 \times 1 \times 10^{-6}} = 157.89$$

$$Ta = \frac{w \,(rad/s) \, r^2}{v} = \frac{600 \times 2\pi \times 0.19^2}{60 \times 1 \times 10^{-6}} = 2.27 \times 10^6$$

$$R* = \frac{r}{r_i} = \frac{0.19}{0.03} = 6.33$$

$$\therefore Sh = 12.57$$

Also $Sh = \dfrac{k_L \delta}{D}$ where $D_{20^\circ C} = 1.74 \times 10^{-5} \; cm^2/sec$

and $\delta = (\frac{3}{2\pi})^{\frac{1}{3}} (\frac{Q \, v}{w^2 r^2})^{\frac{1}{3}}$

$$= (\frac{3}{2\pi})^{\frac{1}{3}} \left[\frac{0.00003 \times 1 \times 10^{-6} \times 60^2}{(600 \times 2\pi)^2 \times 0.19^2} \right]^{\frac{1}{3}}$$

$$= 4.65 \times 10^{-5} \; m$$

$$\therefore k_L = \frac{ShD}{\delta} = \frac{12.57 \times 1.74 \times 10^{-5} \,(cm^2/s) \times 10^{-4}}{4.65 \times 10^{-5}}$$

$$= 4.70 \times 10^{-4} \; m/s$$

Calculation of the Experimental Mass Transfer Coefficient

The mass transfer coefficients were calculated using the equation:

$$\frac{k_L A}{Q} = \ln \frac{C_{eq} - C_1}{C_{eq} - C_2}$$

where k_L = mass transfer coefficient for liquid film controlled mass transfer (ms^{-1})

A = Interfacial area (m^2)

Q = Volumetric flow rate of water ($m^3 s^{-1}$)

C_1 = Concentration of ozone in the inlet water

C_2 = Concentration of ozone in the outlet water

C_{eq} = Equilibrium concentration of ozone in water at $20^\circ C$.

$$k_L = \frac{Q}{A} \ln \frac{C_{eq}}{C_{eq} - C_2} \qquad \text{Since } C_1 = 0$$

$$Q = 3 \times 10^{-5} \ m^3/s$$

$$A = \pi (0.19)^2 - \pi (0.03)^2 = 0.11 \ m^2$$

$$k_L = 2.73 \times 10^{-4} \ \ln \frac{C_{eq}}{C_{eq} - C_2}$$

In this research, samples for dissolved ozone analysis were taken after the disc. Previous mass transfer experiments using oxygen/water and a similar size disc have shown that under the same hydrodynamic conditions (30 cc/s, 600 rpm), about 90% of the total mass transfer occurred on the disc, Lim (39). Hence the ozone concentration at the edge of the disc could be estimated by taking 90% of the actual measured ozone concentration. This value is then used to calculate the mass transfer coefficient of ozone at the edge of the disc.

Appendix C

Possible Inventions

The Higee principle of enhanced mass transfer in rotating devices has been patented previously by:-

C. Ramshaw and J.E. Porter   (Mr. Porter works in these laboratories)

European Patent Application   82306049. 6 Dec.1982

European Patent Application   82306129. 6 Dec.1982

U.K. Patent Application   32836.   Nov.1982

The use of U.V. radiation and ozone in conjunction with this principle for disinfection or refractory treatment may be considered as novel, but it is doubtful if it is patentable because the U.V. and ozone work is well established but with conventional mass transfer processes. There may be scope for a patent with specific processes and thus this topic is included in the Final Invention Report.